



Corrosion Engineering, Science and Technology

The International Journal of Corrosion Processes and Corrosion Control

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/ycst20

Analysis of metal corrosion methods and identification of cost-efficient and low corrosion deicing agents

Michael R. Gruber, Bernhard Hofko, Markus Hoffmann, David Stinglmayr & Hinrich Grothe

To cite this article: Michael R. Gruber, Bernhard Hofko, Markus Hoffmann, David Stinglmayr & Hinrich Grothe (2023): Analysis of metal corrosion methods and identification of costefficient and low corrosion deicing agents, Corrosion Engineering, Science and Technology, DOI: 10.1080/1478422X.2023.2200008

To link to this article: https://doi.org/10.1080/1478422X.2023.2200008

© 2023 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group



Published online: 26 Apr 2023.

|--|

Submit your article to this journal 🖸



🜔 View related articles 🗹



View Crossmark data 🗹

RESEARCH ARTICLE

OPEN ACCESS

Taylor & Francis

Analysis of metal corrosion methods and identification of cost-efficient and low corrosion deicing agents

Michael R. Gruber ^(b)^a, Bernhard Hofko ^(b)^a, Markus Hoffmann ^(b)^{a,b}, David Stinglmayr^c and Hinrich Grothe ^(b)^c

^aInstitute of Transportation, TU Wien, Vienna, Austria; ^bHoffmann Consult e.U., Vienna, Austria; ^CInstitute of Materials Chemistry, TU Wien, Vienna, Austria Austria

ABSTRACT

Deicing agents in winter maintenance are critical in providing safe roads at all times. Sodium chloride (SC) is the most common, efficient and favourable agent but has a drawback of high corrosiveness, thus substantially shortening the service life of metal-based transport infrastructures. This work focuses on corrosion and addresses approaches for the following corrosion test methods that quantify the mass loss of metals for different deicing agents: standardised neutral salt spray test (ISO 9227), salt solution immersion test (ASTM G31-72) and alternate immersion test (ISO 11130). A wide range of different deicing agents with and without corrosion inhibitors are tested on unalloyed steel, and an analytical and visual comparison is made. Results reveal a substantially reduced corrosion effect at reasonable costs by selecting the appropriate deicing agent with or without corrosion inhibitors. For the final selection of deicers, deicing performance and cost-effectiveness are compared.

ARTICLE HISTORY Received 11 October 2022 Accepted 31 March 2023

KEYWORDS

corrosion; alternate immersion; neutral salt spray; unalloyed steel; deicing performance; deicing agents; winter maintenance

Introduction

The main goal of winter maintenance is to guarantee the full accessibility and safety of transport infrastructure during winter periods by providing an adequate level of skid resistance. This goal is achieved mainly by snow plowing and spreading of gritting materials or deicing agents in case of hoarfrost, snowfall events, or freezing rain. With gritting as the main method for low-volume roads and pedestrian walkways with limited lasting effects, the usage of deicing agents is the current standard in most areas of transport infrastructure [1]. According to the criteria of availability, costs and deicing performance, sodium chloride (nontechnical abbreviation is SC, for other abbr. see Table 9) is by far the most cost-effective deicer and is the most used deicing agent in developed countries with regular winter maintenance [2]. However, corrosion is one of the main factors in the reduced service life of transport infrastructure consisting of metals (mostly painted steel and weathering steel) and reinforced concrete [3-6]. Since deicing agents, such as SC, are highly corrosive, a significant reduction in corrosivity would lead to significant savings in investments and energy.

To find alternative deicing agents, a holistic evaluation is required [7]. However, this work focuses on cost effectiveness and corrosion by comparing the deicing performance and mass loss due to corrosion of different deicing agents. In addition to SC and other common acetate-, carbonate-, chloride- and formate-based deicing agents, sugars are tested as inhibitory substances to SC mainly because of their nonhazardous characteristics. The first part of this paper compares the repeatability of three corrosion test methods that are based on, but do not strictly follow, the corresponding standard: (i) standardised neutral salt spray test (ISO 9227) [8], (ii) salt solution immersion test (ASTM G31-72) [9] and (iii) alternate immersion test (ISO 11130) [10]. In the second part, optical results and mass loss due to corrosion on unalloyed steel are investigated for all known principal deicers and selected inhibitors. Finally, the paper concludes with a comparison of corrosivity and cost effectiveness among all tested substances. Effectiveness is determined by deicing performance, which was evaluated using a newly developed method introduced in a separate paper (see section 5) [11].

Institute of Materials

Minerals & Mining

Quantitative assessment of corrosivity is crucial to judge the influence of different deicing agents on corrosion and resulting service life. In general, corrosion in atmospheric environment is controlled by the diffusion rate of oxygen through each barrier present on the reactive steel surface. Thus, corrosion strongly depends on oxygen exposure and temperature. The latter dependence is non-linear since on one hand corrosion multiplies with increasing temperature due to the overcome of the Arrhenius activation barrier, but on the other hand, corrosion also increases with decreasing temperature due to the greater dissolved oxygen content in the aqueous phase at low temperatures (14 mg O_2 per L H₂O at 0°C, 7 mg/L at 35°C) [12-20]. Interestingly, oxygen is essential for depassivation but corrosion progression can also proceed without further oxygen supply [21]. For SC solutions between 2 and 6 wt-% concentrations and exposure time of 10-16 days, it was found that oxygen solubility is higher in lowly concentrated SC solutions than in highly concentrated ones [13]. Another important parameter is conductivity of the environment resulting from the mobile ions: Higher conductance implies higher corrosion rates. Carbon steel is passive at pH higher than approximately 10 but will start to corrode where the chloride-to-hydroxide ration exceeds certain values and when the concrete is carbonated so that the pH is lower than approximately 9 [14,21].

CONTACT Michael R. Gruber 🖾 michael.gruber@tuwien.ac.at 💽 Institute of Transportation, TU Wien, Karlsplatz 13/E230-3, 1040 Vienna, Austria © 2023 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

Some studies have already assessed different corrosion tests with SC. For the full immersion test (FI) a mass loss of 0.6 wt-% due to corrosion was achieved after a total exposure time of 127 days [22], revealing the unsatisfactory performance of this method due to the lack of oxygen [22,23]. A 72-hour alternate immersion test (AI) showed high corrosion rates with 5 wt-% mass loss [19] with SC solutions between 3 and 5 wt-%. At the same time, these high corrosion rates mean that the results cannot be directly applied to real-life applications [24].

Repeatable results in corrosion testing are of particular importance to provide a stable testing environment. For the reliable assessment of different deicers and the effects of inhibitors, significant corrosion effects are necessary to avoid high data scatter related to measurement and handling inaccuracies. Thus, the three corrosion test methods are analysed by comparing the corrosion rates of 5 wt-% SC solutions on unalloyed steel (according to EN 10025 S235JR) [25] specimens ($150 \times 100 \times 1$ mm, 235 ± 2.4 g).

Corrosion methods and identification

In the next sections, the following three test methods that quantify the mass loss due to corrosion on unalloyed steel for different solutions are introduced and compared: (i) standardised neutral salt spray test (ISO 9227) [8], (ii) salt solution immersion test (ASTM G31-72) [9] and (iii) alternate immersion test (ISO 11130) [10].

Neutral salt spray tests - NSS*

The ISO 9227 standard (corrosion test in artificial atmospheres – salt spray tests) [8] specifies three procedures to assess corrosion resistance. Among them, the standardised neutral salt spray (NSS), in which metal specimens ($150 \times 70 \times 1 \text{ mm}$) are wetted by continuous misting (indirect spraying) 5 wt-% SC solution at a temperature of $35 \pm 2^{\circ}$ C between 2 and 1008 h.

For simplification, the reproduced test method (Figure 1) is altered as stated in Table 1 with the main modifications being non-continuous spraying to achieve higher oxygen

exposure and direct spraying of the specimens to increase surface wetting. The modified test method is referred to as NSS*, where the asterisk (*) indicates that it is based on but does not strictly comply to the standardised NSS method in ISO 9227.

Salt solution full immersion tests – FI

In accordance with ASTM G31-72 standard (laboratory immersion corrosion testing of metals) [9], specimens are immersed into a test solution for 48–168 h. Owing to the simplicity of the test method (see scheme in Figure 2), almost no alterations are made for the test as seen in Table 2.

Alternate salt solution immersion tests - Al

The ISO 11130 standard (corrosion of metals and alloys – alternate immersion test in a salt solution) [10] specifies another procedure to assess corrosion resistance. In this method, specimens are repeatedly immersed in a testing solution and dried for specific periods. For standard testing, 3.38 wt-% SC solution is filled into a specimen cabinet. The specimens should be completely immersed at least 10 mm below the solution's surface. The concentration is retained by adding deionised water to counteract evaporation. Every 168 h, the solution is entirely replaced. The specimens are immersed for 10 min and dried for 50 min,

Table 1. Modification of the test method used to ISO 9227.

| | Test according to ISO 9227 | |
|------------------------|-----------------------------------|--|
| | [8] | Modified test [Figure 1] |
| Spraying method | Specimen indirectly sprayed on | Specimen directly sprayed on |
| Spraying duration | Continuous spraying | Non-continuous spraying: 115–117 min spraying 3–5 min drying |
| Test solution | 5% SC, must not be reused | 5% SC, reused |
| Temperature | 35 ± 2°C | 19 ± 1°C |
| Specimen dimension | 150 × 70 × 1 mm – | 150 × 100 × 1 mm 235 ± 2.4 g |
| Number of specimens | ≥4 | 12 |
| Test duration | 2–1008 h | 504 h (21 days) |



Figure 1. Testing device for neutral spray test (NSS*).



Figure 2. Testing device for full immersion (FI) test.

Table 2. Modification of the test method used to ASTM G31-72.

| | Test according to ASTM G31- 72 [9] | Reproduced test [Figure 2] |
|------------------------|---------------------------------------|---------------------------------|
| Test solution | –, 0.5–5 L | 5% SC, 3 L |
| Temperature | _ | 22 ± 1°C |
| Specimen dimension | circular 38 × 3 mm - | 150 × 100 × 1 mm 235 ± 2.4 g |
| Number of specimens | - | 1 |
| Test duration | 48–168 h (2–7 days) | 504 h (21 days) |

| altogether being exposed from 20 to 90 days. Af |
|---|
|---|

Table 3. Modification of the test method used to ISO 11130.

| | Test according to ISO 11130 [10] | Reproduced test [Figure 3] | |
|---------------------------|-------------------------------------|--|--|
| Specimen immersion | 10 min immersed 50 min drying | 10 min immersed 50 min drying | |
| Test solution exchange | Every 7 days | Every 7 days | |
| Test solution | 3.38% SC | 5% SC, 8 L | |
| Temperature solution | 25 ± 2°C | - | |
| Temperature / RH air | $70 \pm 2^{\circ}$ C, $\leq 50\%$ | RT: $19 \pm 1^{\circ}$ C, $32 \pm 5\%$ CC: $34 \pm 1^{\circ}$ C, $>70\%$ CT: $34 \pm 1^{\circ}$ C, $\le 80 \pm 10\%$ | |
| Specimen dimension | 120 × 90 × 1 mm – | 150 × 100 × 1 mm 235 ± 2.4 g | |
| Number of specimens | ≥3 | 12 (3 in 4 cabinets) | |
| Test duration | 20–90 days | 504 h (21 days) | |

thoroughly cleaning and drying, the mass loss is determined at the end of the test. For overall cleaning and handling of specimens, it is referred to ISO 8407 [26]. Differences in the reproduced test method used in this paper compared to ISO 11130 are shown in Table 3 and include testing at different temperatures: Room temperature (RT) and elevated temperature in a climate chamber (CC) and temperaturecontrolled container (CT). A scheme of the apparatus is provided in Figure 3.

Procedure for the determination of corrosion mass loss

The correct determination of mass loss due to corrosion is crucial for comparing different test methods, especially when low rates of corrosion are produced. Therefore, the ISO 8407 standard (corrosion of metals and alloys – removal of corrosion products) [26] is followed. Light mechanical treatment by brushing is recommended. For further cleaning, chemical, electrolytic and vigorous mechanical treatments are applied until mass consistency is achieved. The use of 20 wt-% diammonium hydrogen citrate solution in an ultrasonic bath has shown the best repeatability for cleaning the samples of corrosion products. Mechanical procedures, such as scaping, scrubbing, brushing and grit blasting, have low costs but may lead to biased results because the removal of corrosion products may not be performed uniformly.

In this work, the suggested combination of (light) mechanical and chemical cleaning with the help of an ultrasonic bath is used. After the end of each test period, all specimens are cleaned with tap water, and adherent corrosion products are removed by gently dabbing with a paper towel. Up to 9 specimens are thoroughly cleaned in an ultrasonic bath (see Figure 4) with a 20 wt-% diammonium hydrogen citrate solution at 50°C for 30 min and then dabbed dry with a paper towel and weighed. This step is repeated (time in the ultrasonic bath is reduced to 10 min after an initial run with 30 min) until mass consistency is achieved. Relative mass loss is calculated by dividing the total mass loss by the initial mass of the specimen ($150 \times 100 \times 1 \text{ mm}$, $235 \pm 2.4 \text{ g}$) before the test using Equation (1). On the basis of the results of this procedure, a high level of repeatability is achieved compared



Figure 3. Testing device for alternate immersion (AI) test.



Figure 4. Ultrasonic bath with 20 wt-% diammonium hydrogen citrate.

with that in the other methods.

relative mass loss [wt%] =
$$\frac{m_{\text{before}} - m_{\text{after}}}{m_{\text{before}}} \times 100$$
 (1)

Test schedule for the comparison of corrosion methods

As stated in ISO 11130 [10], corrosion is influenced by many factors and can vary significantly under different conditions. Consequently, the AI, FI and NSS* tests are not directly applicable to real-life situations. Tests conducted under real-life conditions (e.g. temperatures below freezing, long

| Table 4. Testing | g conditions for 5 wt-% | SC solution of all cor | rosion methods. |
|------------------|-------------------------|------------------------|-----------------|
| | | | |

| Category | Test method | Test environment | Temperature | Relative humidity | Cycle period | Specimens | |
|----------|---------------------|----------------------|------------------|-------------------|-------------------------------------|-----------|--|
| Al@CC | Alternate immersion | Climate chamber | 34.25°C ± 0.68°C | est. >70% | 1 h: 10 min immersed, 50 min drying | 12 | |
| Al@CT | Alternate immersion | Container tempcontr. | 34.24°C ± 0.72°C | 79.47% ± 8.61% | 1 h: 10 min immersed, 50 min drying | 23 | |
| AI@RT | Alternate immersion | Room temperature | 18.72°C ± 0.72°C | 32.12% ± 4.67% | 1 h: 10 min immersed, 50 min drying | 12 | |
| FI@RT | Full immersion | Room temperature | 21.87°C ± 0.95°C | NA | 21 days immersed | 5 | |
| NSS*@RT | Neutral salt spray | Room temperature | 19.15℃ ± 0.79℃ | 33.73% ± 7.69% | 2 h: 3 min spraying, 117 min drying | 15 | |





Alternate immersion in climate chamber Al@CC



Alternate immersion in temp.-contr. container Al@CT



Room temperature

Alternate immersion at room temp. Al@RT



Full immersion at room temp. FI@RT



Neutral salt spray at room temp. NSS*@RT

immersion and drying periods) would lead to a substantial increase in test duration, rendering any test programme inefficient and expensive.

Table 4 provides an overview of the test methods and their surrounding conditions. All tests are conducted with a 5 wt-% SC solution on unalloyed steel (EN 10025 S235JR [25]).

For the AI test, two different ambient temperatures, namely, room temperature (AI@RT) and elevated temperature $34 \pm 1^{\circ}$ C, are investigated in a climate chamber (AI@CC). A large number of specimens are simultaneously tested in a 10-feet temperature-controlled container (AI@CT). For these tests, the immersion cycle is 1 h, with 10 min of fully immersing the specimens in 5 wt-% SC solution and 50 min of drying.

For the FI test, the specimens are immersed for 21 days at room temperature (FI@RT). The ambient temperature is slightly higher $(22 \pm 1^{\circ}C)$ than that in other tests at room temperature $(19 \pm 1^{\circ}C)$ because the system allows only minimal air exchange with the surrounding environment.

For the NSS^{*} test, three cabinets are built in which the specimens are exposed to a 2-hour cycle consisting of 3 min of spraying 5 wt-% SC solution, followed by 117 min of drying at room temperature (NSS*@RT). This cycle is chosen to maintain a throughput of 30 L of solution daily. An overview of the methods stated in Table 4 can be found in Figure 5.

Analytical comparison of corrosion test methods and applicability

A comparison of the results from different methods as boxplots with marked outliers outside of the maximum whisker length of 1.5-times the interquartile range (IQR) can be found in Figure 6. The FI test method exhibits minimal effect on corrosion presumably due to low aeration [12– 14,21,22]. The total mass loss is 0.2 wt-% (0.5 g) after 21 days; handling errors and cleaning procedure might have significantly biased the results. All other test methods produce a higher level of mass loss at room temperature but low corrosion effects to avoid the significant impacts of handling and cleaning errors. The NSS* test method showed problems with clogged spraying nozzles, possibly caused by reusing the solution and precipitation of salt inside the nozzles caused by not sufficiently humifying incoming air (both alterations to the standard NSS test according to ISO 9227). In addition to these problems, the NSS* test spreads aerosols containing SC, which might cause corrosion of the surrounding materials. Consequently, testing at high temperatures in a climate chamber or temperature-controlled container is not a feasible option due to the expected damages. Thus, the AI test remained as the only feasible method for testing inside the climate chamber.

Tests inside the climate chamber reveal significant variance (interquartile range IQR of 4.7 wt-% at a median of 11.7 wt-% or 27.4 g mass loss) probably induced by the irregular strong air flow generated by the air conditioning unit to maintain the temperature level. The size of the climate chamber accommodates just one testing device (containing 12 specimens), limiting the number of tests in a given time.

Therefore, a 10-feet temperature-controlled container is used to hold three devices, allowing for the simultaneous testing of 36 specimens (test setup shown in Figure 8). The results for 23 specimens (obtained at three different series of 21 days) show smaller variance compared to those in the climate chamber (IQR of 0.8 wt-% at a median of 14.2 wt-% or 33.2 g mass loss).

Optical comparison of corrosion tests

A visual comparison of the specimens before testing (5 wt-% SC solution on unalloyed steel), after 21 days testing, and



Figure 6. Results of all test methods with 5 wt-% SC solution.



Figure 7. Optical comparison of the specimens before and after testing with 5 wt-% SC solution.



Figure 8. Test setup inside the temperature-controlled container (Al@CT).

after cleaning for all test methods can be seen in Figure 7. Similar to the results in Figure 6, differences among the high corrosion effects of the AI test at high temperature, the medium effects of the AI test at room temperature and the low effects of all other test methods can be observed. The high corrosion effects for AI test in the container compared with that in the climate chamber can be explained by the high relative humidity inside the container and the irregular strong airflow inside the climate chamber.

| Table 5. Tested deicing agents without added inhibitory substances. | |
|--|--|
|--|--|

| Agent | Abbr. | Sol. [wt-%] | Formula | Specimens |
|---------------------|-------|-------------|--------------------------------|-----------|
| Sodium chloride | SC | 5 | NaCl | 38 |
| Potassium carbonate | PC | 5 | K ₂ CO ₃ | 6 |
| Calcium chloride | CC | 5 | CaCl ₂ | 6 |
| Magnesium chloride | MC | 5 | MgCl ₂ | 6 |
| Sodium acetate | SA | 5 | CH ₃ COONa | 6 |
| Sodium formate | SF | 5 | HCOONa | 6 |
| Potassium acetate | PA | 5 | CH₃COOK | 6 |
| Potassium formate | PF | 5 | HCOOK | 6 |

Table 6. Test schedule of SC with different concentrations of glucose.

| | | | 5 | |
|-----------|----------------|------------|-----------------------|---------|
| Agent | Inhibitor | Abbrev. | Formula | Specim. |
| SC 5 wt-% | Glucose 2 wt-% | SC + 2%Glu | $NaCI + C_6H_{12}O_6$ | 6 |
| SC 5 wt-% | Glucose 4 wt-% | SC + 4%Glu | $NaCl + C_6H_{12}O_6$ | 6 |
| SC 5 wt-% | Glucose 6 wt-% | SC + 6%Glu | $NaCl + C_6H_{12}O_6$ | 6 |
| SC 5 wt-% | Glucose 8 wt-% | SC + 8%Glu | $NaCl + C_6H_{12}O_6$ | 6 |

Table 7. Test schedule of SC with different sugars.

| - | | | | |
|-----------|------------------|------------|-----------------------------|---------|
| Agent | Inhibitor | Abbrev. | Formula | Specim. |
| SC 5 wt-% | Arabinose 8 wt-% | SC + 8%Ara | $NaCl + C_5H_{10}O_5$ | 6 |
| SC 5 wt-% | Glucose 8 wt-% | SC + 8%Glu | $NaCI + C_6H_{12}O_6$ | 6 |
| SC 5 wt-% | Maltose 8 wt-% | SC + 8%Mal | $NaCl + C_{12}H_{22}O_{11}$ | 6 |
| SC 5 wt-% | Mannose 8 wt-% | SC + 8%Man | $NaCl + C_6H_{12}O_6$ | 6 |
| | | | | |

Corrosion of deicing agents and inhibitors

Given that the AI test inside the temperature-controlled container (AI@CT) shows the highest corrosion products and good repeatability, this setup is used to classify the corrosion effects of other deicing agents (as anhydrate) on unalloyed steel (EN 10025 S235JR) [25]. Figure 8 shows the test setup inside the container. Table 5 shows the testing schedule for the deicing agents in a 5 wt-% solution and introduces nontechnical abbreviations (e.g. PA = Potassium acetate = CH₃. COOK) for improved readability, especially in figures. Given that most alternative deicing agents are quite expensive compared with SC, another option is to add a small amount of (possibly expensive) corrosion inhibitor to (rather inexpensive) SC. Therfore, glucose is tested with different concentrations of 2 wt%, 4 wt-%, 6 wt-% and 8 wt-% to identify the effect of different concentrations on corrosion (Table 6). The concentration of the inhibitor is based on the dry mass of SC, that is, 1000 g of 5 wt-% SC solution (50 g of SC and 950 g of water) 2 wt-% of the inhibitor (2 wt-% of 50 g = 1 g) are added.

Other sugars such as arabinose, maltose and mannose are also tested as corrosion inhibitors with a dosage of 8 wt-% of the mass of SC. The corresponding test schedule can be seen in Table 7.

Analytical comparison

After 21 days of exposure to the AI test inside the temperature-controlled container (AI@CT) and cleaning until mass consistency is achieved, the resulting relative mass loss is displayed as boxplots in Figure 9. SC has the highest mass loss due to corrosion on unalloyed steel of around 14.2 wt-% (33.2 g). The mass loss of other deicing agents ranges from 3 wt-% (7.0 g) to 6 wt-% (14.1 g), except



Figure 9. Results of all tested main deicing agents.



Figure 10. Results of different dosages of glucose (left) and of different sugars (right).



Figure 11. Optical comparison of the specimen before and after testing (deicing agents).

potassium formate (PF) (10.2 wt-% or 24.0 g) and potassium carbonate (PC) (0.9 wt-% or 2.1 g). PC provides better protection compared to water (H_2O : with 2.1 wt-% or

4.9 g), as it forms an alkaline solution leading to a passivation of the steel surface and consequently to reduced corrosion.



Figure 12. Optical comparison of the specimen before and after testing (glucose).

The left part of Figure 10 shows the results of the testing schedule according to Table 6. As expected, an increase in the amount of glucose added to SC leads to a decrease in corrosion. This positive effect starts to flatten with an 8 wt-% dosage, indicating an optimal dosage from an economic point of view. Therefore, 8 wt-% dosage is chosen as a reference to test other sugars as stated in Table 7. The right part of Figure 10 shows that arabinose and glucose reduce the corrosion products by around 50%, and mannose performs better with 60% reduction compared with SC. By contrast, maltose only allows for a 30% reduction in corrosion.

Optical comparison

In addition to the analytical comparison, Figure 11 shows the specimens before and after testing in a 5 wt-% solution. SC has the most corrosive effect on the unalloyed steel, and PC has the least. All other deicing agents are somewhere in between. A difference in corrosion pattern is observed between magnesium chloride (MC) and potassium acetate (PA).

The set of tests comparing the corrosion of SC (as a 5 wt-% solution) with an inhibitor added (percentage related to the amount of SC) in Table 6 are shown in Figure 12. Glucose is tested at 2, 4, 6 and 8 wt-% to identify the increase in inhibitory effect with the amount of the substance added. This effect can be

seen but at high amounts, only minimal difference can be spotted.

All other tested sugars in Table 7 can be seen in Figure 13. A reliable optical differentiation is not possible, sincecorrosion reduction is in a narrow range between 40% and 60% compared SC.

Acquisition costs

Given that cost-effectiveness is the main factor for choosing deicing agents, the market prices for all main agents are surveyed. Apart from principal availability in considerable quantities, the unit prices decrease sharply with the increasing amounts [7]. This phenomenon is called economy of scales, an example for SC can be seen in Figure 14. In addition, the provided data from the market analysis may vary because of considerable seasonal and regional fluctuations regarding prices and availability. Table 8 lists the prices in Euro (Central Europe 2021) of the main deicing agents per metric ton when buying large quantities (\gg 10 tons). The last column shows the relative price to SC (=100%). This image is a snapshot and probably no longer accurate due to the strong fluctuations in prices and currency exchange rates caused by the COVID pandemic and the war in Europe.



Figure 13. Optical comparison of the specimen before and after testing (all sugars).

Comparison of corrosion and cost efficiency

The primary purpose of deicing in winter maintenance is to provide a sufficient level of skid resistance by avoiding freezing due to preventive spreading or to remove residual snow and ice by applying deicing agents. The necessary amount for the latter is determined by the deicing performance, which states the amount of ice or snow that can be deiced (in grams ice per gram deicing agent, g/g) at a given temperature. Given that deicing performance is largely based on the freezing curve, it decreases for all deicers at low temperatures.

For cost-efficient winter maintenance, the deicing performance and costs of relevant deicing agents or products consisting of primary deicers, additives and impurities must be determined. The deicing performance was investigated in a separate paper [11], in which a non-linear model was derived from the results of a newly developed



Table 8. Prices (>10 t) of deicing agents and inhibitors (Central Europe 2021).

| Agent | Formula | Abbrev. | Price [€/ton] | Relat. costs to SC [%] |
|--------------------------------|--------------------------------------|---------|------------------|---------------------------|
| Calcium chloride | $CaCl_2 \cdot 2H_2O$ | CC | 170 | 142 |
| Potassium carbonate | K ₂ CO ₂ | PC | 900 | 750 |
| Potassium acetate | CH₃COOK | PA | 600 | 500 |
| Potassium formate | нсоок | PF | 700 | 583 |
| Magnesium chloride (hexah.) | MgCl ₂ .6H ₂ O | MC | 250 | 208 |
| Sodium acetate | CH ₃ COONa | SA | 250 | 208 |
| Sodium chloride | NaCl | SC | 120 | Base = 100 |
| Sodium chloride + | NaCI + | SC + 8% | 155 | 129 |
| 8 wt-% arabinose | $C_5H_{10}O_5$ | Ara | | |
| Sodium chloride + | NaCI + | SC + 8% | 155 | 129 |
| 8 wt-% glucose | $C_6H_{12}O_6$ | Glu | | |
| Sodium chloride + | NaCI + | SC + 8% | 155 | 129 |
| 8 wt-% maltose | $C_{12}H_{22}O_{11}$ | Mal | | |
| Sodium chloride + | NaCI + | SC + 8% | 155 | 129 |
| 8 wt-% mannose | $C_6H_{12}O_6$ | Man | | |
| Sodium formate | HCOONa | SF | 250 | 208 |

Table 9. Deicing performance obtained from CEDA after 300 Min at -5°C [11].

| Agent | Abbr. | Deicing perf. [g/g] |
|--|-------------|---------------------|
| Sodium chloride | SC | 12.75 |
| Potassium carbonate | PC | 6.74 |
| Calcium chloride dihydrate | CC | 8.28 |
| Magnesium chloride hexahydrate | MC | 6.83 |
| Sodium acetate | SA | 8.16 |
| Sodium formate | SF | 11.41 |
| Potassium acetate | PA | 10.59 |
| Potassium formate | PF | 6.38 |
| Sodium chloride + 8 wt-% arabinose | SC + Ara | 11.63 |
| Sodium chloride + 8 wt-% glucose | SC + Glu | 11.62 |
| Sodium chloride + 8 wt-% maltose monohydr. | SC + Mal | 11.75 |
| Sodium chloride + 8 wt-% mannose | SC + Man | 10.37 |

method for testing deicing performance (called CEDA). CEDA shows the time-temperature dependency of the deicing performance, allowing for reliable predictions of the necessary amounts of deicers for any given situation. Table 9 gives an overview of the deicing performance of different deicing agents after 300 min exposure at -5° C.

In addition to the deicing performance, the market price is a key factor in the decision-making process. However, with focus beyond winter maintenance on highly expensive transport infrastructure consisting of metals and reinforced concrete (e.g. train stations, bridges, airports), corrosion also becomes a decisive factor from a life cycle perspective. Thus, the left part of Figure 15 shows a comparison of relative mass loss due to corrosion and costs per ton of ice melted among all tested deicing agents with and without inhibitory substances (at -5° C).

For example, SC (colour: aquamarine) is highly corrosive but a cost-effective deicing agent and thus is placed on the top left of the diagram. By contrast, PC (colour: green) produces minor corrosion but is rather expensive and is therefore placed on the bottom right. A comparison of corrosion and deicing performance (at -5° C) without considering costs is provided in the right part of Figure 15. The figure shows that PC (colour: green) has the same deicing performance as PF (colour: burgundy) but produces only one-fifth of its corrosion. In general, both figures are structured in a way that the best performing deicing agents are at the bottom left of the diagram, the *y*-axis displays relative mass loss [wt-%], and the *x*-axis shows costs per ton of ice melted (Figure 15 left) or deicing performance at 300 min of exposure (Figure 15 right).

Conclusions and outlook

Deicing agents in winter road maintenance are critical in providing safe roads at all times. Beyond winter maintenance, SC as main deicer is highly corrosive and substantially shortens the service life of transport infrastructures. Therefore, cost-efficient alternatives or ways to reduce corrosion effects without diminishing the road safety are the key to saving billions of transport infrastructure investments every year on a worldwide scale. This paper presents the results of extensive research and analysis of the essential criteria of deicing agents: deicing performance, corrosion on metals and costs.

A comparative analysis of the three commonly used test methods to reproduce corrosion effects is conducted to quantify the mass loss of unalloyed steel exposed to deicing agents. All test methods are generally based on the corresponding standard but have been modified to reduce the testing effort. FI test has led to barely measurable mass loss, and NSS* test is unreliable due to the clogging of spraying nozzles (presumably due to modifications to the standard ISO 9227). AI test produces the highest quantity of corrosive products at an elevated temperature of $+34 \pm 1^{\circ}$ C with a high level of repeatability. With this method, all relevant main deicing agents can be tested. In addition, corrosion inhibitors such



Figure 15. Comparison of corrosion (ordinate) and costs (left) or deicing performance (right) [11].

as sugars are added to SC to identify their impact on reducing corrosion at different dosages.

Since the procedure of determining mass loss is significant for comparable results, a gentle mechanical cleaning in combination with chemical cleaning in an ultrasonic bath until mass consistency using a 20 wt-% solution of diammonium citrate (ISO 8407) was used and led to accurate results. According to the comparison of the relative mass loss of different deicing agents, PC causes the passivation of steel and has therefore the least corrosive effect on unalloyed steel (specimens $150 \times 100 \times 1$ mm, 235 g) with 0.9 wt-% (2.1 g) mass loss compared with 14.2 wt-% (33.4 g) of SC. For a mixture of (inexpensive) SC with only a minor (8 wt-% based on the mass of SC) corrosion inhibitor, the monosaccharide glucose has a significant effect and reduces mass loss by half from 14 wt-% to nearly 7 wt-%. Other monosaccharides (arabinose, maltose and mannose) show similar results.

In summary, sufficient reduction in corrosion rates can be achieved either by choosing a different deicing agent or by adding an inhibitory substance such as a monosaccharide. An answer to which primary deicing agent or combination of deicing agents and corrosion inhibitors can provide the best overall performance is illustrated in this research. For limited areas of application with high unit costs, such as train stations, using alternative deicers or corrosion inhibitors is usually cost-effective. In general, the selection of the most suitable deicing agent or inhibitors, or both, depends largely on whether the additional costs for the deicing agent producing similar deicing performance are outweighed by the savings due to increased service life. The next stepsare the identification and testing of additional inhibitors and materials. Nevertheless, the methods and results in the current work provide concise answers and a clear path for future research toward cost-effective deicing agents with significantly lower corrosion than SC.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The research was made possible by the project WINTER-LIFE (Österreichische Forschungsförderungsgesellschaft) [FFG-Project No. 873169] as part of the programme 'Mobility for the Future' and would not have been possible without the funding from the Austrian Research Promotion Agency (FFG) and the Austrian Federal Railways (OEBB) and builds on the experience from several previous research projects of TU Wien and Hoffmann Consult in the field that has been funded by the State Road Agencies, ASFINAG and the Federal Ministry for many years. The authors also acknowledge TU Wien Bibliothek for financial support through its Open Access Funding Program and for financial support for editing/proofreading.

ORCID

Michael R. Gruber http://orcid.org/0000-0002-6179-7565 Bernhard Hofko http://orcid.org/0000-0002-8329-8687 Markus Hoffmann http://orcid.org/0000-0003-2690-1192 Hinrich Grothe http://orcid.org/0000-0002-2715-1429

References

 Hanke H, Nutz P. International development of application methods of deicing chemicals-state of the art and best practice. France: La Defense; 2019. p. 4–9. ISBN: 978-2-84060-514-0

- [2] PIARC. Snow and Ice Databook 2018-SIDB 2018EN. PIARC Technical Committee B.2 Winter Service; 2019, 25–33.
- [3] Shi X, Veneziano D, Xie N, et al. Use of chloride-based ice control products for sustainable winter maintenance: a balanced perspective. Cold Reg Sci Technol. 2013;86:104–112. doi:10.1016/j. coldregions.2012.11.001.
- [4] Shi X, Jungwirth S, Akin M, et al. Evaluating snow and Ice control chemicals for environmentally sustainable highway maintenance operations. J Transport Eng. 2014;140(11):5014005. doi:10.1061/ (ASCE)TE.1943-5436.0000709.
- [5] Koch GH, Brongers M, Thompson NG et al. Handbook of environmental degradation of materials. Norwich, NY; 2005. doi:10.1016/B978-081551500-5.50003-3.
- [6] Van der Wegen G, Polder RB, Van Breugel K. Guideline for service life design of structural concrete – a performance based approach with regard to chloride induced corrosion. Heron. 2012;57(3):153–168.
- [7] Hoffmann M, Gruber MR, Hofko B, et al. Winterlife: effective, sustainable and non-corrosive deicing agents in winter maintenance. PIARC-XVI World Winter Service and Road Resilience Congress; 2022, Calgary.
- [8] ISO 9227:2017: Corrosion tests in artificial atmospheres-salt spray tests. International Organization for Standardization; 2017. Available from: www.iso.org.
- [9] Astm G31-72(2004): Standard practice for laboratory immersion corrosion testing of metals, West Conshohocken, PA, ASTM International; 2004. Available from: www.astm.org.
- [10] ISO 11130:2017: Corrosion of metals and alloys-alternate immersion test in salt solution. International Organization for Standardization; 2017. Available from: www.iso.org.
- [11] Gruber MR, Hofko B, Hoffmann M, et al. Deicing performance of common deicing agents for winter maintenance with and without corrosion-inhibiting substances. Cold Reg Sci Technol. 2023;208. doi:10.1016/j.coldregions.2023.103795.
- [12] Ismail A, Adan NH. Effect of oxygen concentration on corrosion rate of carbon steel in seawater. Am J Eng Res. 2014;3(1):64–67.
- [13] Boies DB, Bortz S. Economical and effective deicing agents for use on highway structures. Chicago, IL: National Cooperative Highway Research Report (NCHRP); 1965. p. 19.
- [14] Yuan Y, Ji Y, Jiang J. Effect of corrosion layer of steel bar in concrete on time-variant corrosion rate. Mater Struct. 2009;42:1443– 1450. doi:10.1617/s11527-008-9464-9.
- [15] Wang J, Wang J, Ming H, et al. Effect of temperature on corrosion behavior of alloy 690 in high temperature hydrogenated water. J Mater Sci Technol. 2018;34(8):1419–1427.
- [16] Skaperdas GT, Uhlig HH. Corrosion of steel by dissolved carbon dioxide and oxygen. Indus Eng Chem. 1942;34(6):748–754.
- [17] Mercer AD, Lumbard EA. Corrosion of mild steel in water. Br Corros J. 1995;30(1):43–55. doi:10.1179/bcj.1995.30.1.43.
- [18] Tromans D. Modeling oxygen-controlled corrosion of steels in hot waters. Corrosion. 1999;55(10):942–947.
- [19] Speller N. Corrosion, causes, and prevention. 3rd ed. New York: McGraw-Hill; 1951, p. 168.
- [20] Paul S. Estimation of corrosion rate of mild steel in seawater and application of genetic algorithms. Can Metall Q. 2010;45:99–106.
- [21] Andrade C. Correction to: propagation of reinforcement corrosion: principles, testing and modelling. Mater Struct. 2020;53. doi:10.1617/s11527-019-1420-3.
- [22] Callahan M. Deicing salt corrosion with and without inhibitors. Washington, DC: Highway Division, Iowa Department of Transportation; 1988.
- [23] Tempest B, Whelan M, Prah-Enin PK et al. Quantifying corrosive potential of de-icing and anti-icing solutions on bridge components – Final Report, North Carolina Department of Transportation Research Project FHWA/NC/2012-08; 2013.
- [24] Shi X, Fay L, Yang Z, et al. Corrosion of deicers to metals in transportation infrastructure: introduction and recent developments. Corros Rev. 2009;27(1–2):23–52. doi:10.1515/CORRREV.2009.27.1-2.23.
- [25] Austrian Standards. OENORM EN 10025-1:2004: Hot rolled products of structural steels – Part 1: General technical delivery conditions; 2004. Available from: www.austrian-standards.at.
- [26] ISO 8407:2021: Corrosion of metals and alloys-removal of corrosion products from corrosion test specimens. International Organization for Standardization; 2021. Available from: www. iso.org.