

**CORROSION OF DEICERS TO METALS IN TRANSPORTATION
INFRASTRUCTURE: INTRODUCTION AND RECENT DEVELOPMENTS**

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ABSTRACT

Chemicals used in the snow and ice control operations (also known as deicers) may cause corrosion damage to the transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges. This review presents a synthesis of information regarding the impacts of both chloride-based and acetate/formate-based deicers on metals especially steel rebar in concrete, common test methods to quantify such impacts, and countermeasures to manage such impacts. There are many ways to manage the corrosive effects of deicers, such as: selection of high-quality concrete, adequate concrete cover and alternative reinforcement, control of the ingress and accumulation of deleterious species, injection of beneficial species into concrete, and use of non-corrosive deicer alternatives and optimal application rates.

KEYWORDS

Deicer, snow and ice control, reinforcing steel, corrosion, review

1. Introduction

Large amounts of solid and liquid chemicals (known as deicers) as well as abrasives are applied onto winter highways to keep them clear of ice and snow. Deicers applied onto highways often contain chlorides because of their cost-effectiveness, including mainly sodium chloride (NaCl), magnesium chloride (MgCl₂), and calcium chloride (CaCl₂), sometimes blended with proprietary corrosion inhibitors. A recent survey of highway maintenance agencies conducted by our group indicated that NaCl was the most frequently used deicer, followed by abrasives, then MgCl₂, agriculturally based products, CaCl₂, and others. Less than 25% of the survey respondents used alternative deicers such as potassium acetate (KAc), sodium acetate (NaAc), calcium magnesium acetate (CMA), and potassium formate /1/.

In 2007 the U.S. sold approximately 20.2 million tons of deicing salts for use in winter maintenance /2/. The growing use of deicers has raised concerns over their effects on motor vehicles, transportation infrastructure, and the environment /3-6/. Motorists and trucking associations have become wary of deicers on their vehicles, as the vehicular corrosion (even though generally cosmetic) has been documented. On average, the deicer corrosion to each vehicle was estimated to cost \$32 per year /5/. Furthermore, chemicals may cause corrosion damage to the transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges /4/. The deleterious effect of deicing salts on reinforcing steel bar (rebar) in concrete structures is well known /7-9/. A recent study conducted for the U.S. National Cooperative Highway Research Program (NCHRP) identified the deicer corrosion to steel rebar as the primary concern, followed by

detrimental effects to vehicles, concrete in general, structural steel, and roadside structures /10/.

Deicers may also pose detrimental effects on concrete infrastructure through their reactions with the cement paste and thus reduce concrete integrity and strength, which in turn may foster the ingress of moisture, oxygen and other aggressive agents onto the rebar surface and promote the rebar corrosion. The long-term use of NaCl can initiate and/or accelerate alkali-silica reaction (ASR) by supplying additional alkalis to concrete /11-17/, whereas CaCl_2 and MgCl_2 do not have as obvious an effect on ASR as NaCl. Numerous research studies have shown that MgCl_2 , when used as a deicer, causes much more severe deterioration to concrete than NaCl or CaCl_2 . This is due to the reaction between Mg^{2+} and the hydrated products in cement paste /18-22/, which has been reported to be responsible for the degradation of concrete matrix caused by MgCl_2 and CMA /10/. It has also been found that concrete exposed to CaCl_2 deteriorated in a similar pattern to those exposed to MgCl_2 , although at a slower and less severe pace /23/. Both MgCl_2 and CaCl_2 deicers are known to deteriorate concretes containing reactive dolomite aggregates by accelerating the alkali-carbonate reaction /19-20/. Recent research has found that the acetate/formate deicers could induce increased levels of expansion in concrete with ASR-susceptible aggregates, and could trigger ASR in concrete that previously did not show ASR susceptibility /24-26/.

When using chloride-based deicers for snow and ice control, the average cost due to corrosion and environmental effects are estimated at three times as high as the nominal cost /27/. One study has estimated that the use of road salts imposes infrastructure corrosion costs of at least \$615 per ton, vehicular corrosion costs of at least \$113 per ton, aesthetic costs of \$75 per ton if applied near environmentally sensitive areas, in addition to uncertain

human health costs /28/. The estimated cost of installing corrosion protection measures in new bridges and repairing old bridges in the Snowbelt states is between \$250 million and \$650 million annually /29/. Parking garages, pavements, roadside hardware, and non-highway objects near winter maintenance activities are also exposed to the corrosive effects of road salts. It should be noted that any repairs to the infrastructure translate to costs to the user in terms of construction costs, traffic delays and lost productivity. Indirect costs are estimated to be greater than ten times the cost of corrosion maintenance, repair and rehabilitation /30/.

This review paper presents a synthesis of information regarding the corrosion of common deicers to metals in transportation infrastructure, with a focus on steel rebar in concrete structures. The following section documents the corrosion impacts that NaCl, CaCl₂ and MgCl₂ have on metals compared with those of alternative deicers, which is followed by discussions of methods to quantify and manage deicer impacts to metals.

2. Deicer Impacts on Metals

2.1 Chloride-Based Deicer Impacts on Steel Rebar

Chloride ingress, either from marine environments or from chloride-based deicers, is one of the primary forms of environmental attack for reinforced concrete structures /31-32/, which leads to rebar corrosion and a subsequent reduction in the strength, serviceability, and aesthetics of the structure. The chloride permeability of concrete is thus considered a critical intrinsic property of the concrete /33/. The remediation of concrete bridges in the U.S., undertaken as a direct result of chloride-induced rebar corrosion, would cost the U.S. highway departments \$5 billion per year /34/. Premature deterioration of bridge decks, as

well as the contamination of parking garages due to the application of deicing salts has been reported /29/.

In addition to the chloride-induced rebar corrosion, chloride-based deicers can exacerbate the scaling problem and freeze-thaw damage of concrete. The use of properly cured, air-entrained Portland cement concrete, however, can prevent such physical deterioration of concrete. Otherwise, in cold-climate regions, the synergy of freeze-thaw cycles and rebar corrosion may lead to problems against reinforced concrete structures, with serious economic and safety implications.

2.1.1 Mechanism for Chloride-Induced Corrosion of Steel Rebar

Concrete normally provides both chemical and physical protection for the embedded steel reinforcement. The cement hydration leads to the high alkalinity ($\text{pH} \approx 13-14$) of concrete pore solution, which promotes the formation of an approximately 10-nm thick oxide/hydroxide film at the steel surface /35/. This protective passive film effectively insulates the steel and electrolytes so that the corrosion rate of steel is negligible. The concrete cover also prevents or at least retards the ingress of aggressive substances toward the rebar surface.

Localized corrosion of rebar may occur when water and oxygen are available at the steel surface and the passive film is jeopardized by a decrease in the pH of concrete pore solution and/or by the presence of enough water-soluble (free) chloride ions /9/. Chloride-induced corrosion of steel rebar generally proceeds in the following steps /36-39/:

A. Ingress of chloride into the concrete to a point where a threshold chloride concentration is reached at the embedded reinforcement depth.

Corrosive agents (e.g., deicer solution) may penetrate through the concrete via capillary absorption, hydrostatic pressure, or diffusion. The ingress of gases, water or ions dissolved in aqueous solutions into concrete takes place through pore spaces in the cement paste, at the cement paste-aggregate interfaces or through micro-cracks. For the durability of concrete, permeability is believed to be the most important characteristic /40/, which is related to its micro-structural properties, such as the size, distribution, and interconnection of pores and micro-cracks /41/.

It is generally believed that only the free chlorides can promote pitting corrosion, while the bound chlorides such as those adsorbed on C-S-H (calcium silicate hydrate) or chemically bound with concrete C_3A (tricalcium aluminate) or C_4AF phases (e.g., Friedel's salt, $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) do not. However, a recent study suggests that bound chlorides also play a role in corrosion initiation, as a large part of them is released as soon as the pH drops to values below 12/42/. The concentration ratio of free chloride to total chloride in concrete may range from 0.35 to 0.90, depending on the constituents and history of the concrete /43/.

The chloride threshold to initiate active corrosion of steel in concrete has been expressed as the free chloride concentration, total chloride concentration, or chloride-to-hydroxyl concentration ($[Cl^-]/[OH^-]$) ratio. Chloride concentrations as low as 0.6 kg/m^3 in concrete have been projected to compromise steel passivity /35/. Another study reported a threshold total chloride concentration of 0.20 wt% by weight of cement to initiate rebar

corrosion in bridge decks /44/. The $[\text{Cl}^-]/[\text{OH}^-]$ ratio is a more reliable indicator than the chloride concentration, considering that the competition between aggressive Cl^- and inhibitive OH^- governs the pitting/repassivation of steel. The gradual ingress of atmospheric carbon dioxide into the concrete, a process known as carbonation, may jeopardize the passive film by reducing the pH of the concrete pore solution. However, the corrosion due to carbonation progresses at a much slower rate than that due to chloride ingress /45/.

Research in aqueous solutions has indicated that for chloride-contaminated concrete the pitting corrosion occurs only above a critical $[\text{Cl}^-]/[\text{OH}^-]$ ratio /46/. Through a probability simulation model, the threshold $[\text{Cl}^-]/[\text{OH}^-]$ for corrosion of bare steel rods in high pH solutions was once predicted to be 0.66 in the presence of oxygen bubbles attached to the steel and 1.4 in the case of air. Such result agreed favorably with experimental data. In the same model, it was concluded that the threshold ratio should be about 1.4 for typical reinforced concrete and in excess of 3 for high quality concrete with minimal air voids /47/. The chloride threshold generally increases with increasing concrete quality.

B. Local disruption of the passive film and onset of active corrosion in the form of corrosion cells /35, 47/.

The local disruption of the passive film initiates corrosion cells between the active corrosion zones (anode) and the surrounding areas that are still passive (cathode), as shown in Figure 1. In this step, the pit growth can only be sustained above a critical $[\text{Cl}^-]/[\text{OH}^-]$ ratio, or the rebar surface will be re-passivated by forming an iron oxide/hydroxide layer /48/.

As implied in the cathodic and anodic reactions above, aside from pH, temperature and oxygen content play important roles in rebar corrosion. Corrosion of reinforcing steel was found to vary with oxygen contents and temperatures of the corrosion-inhibitor-added deicing salt and salt substitute solutions /49/. Oxygen contents in solutions under the control condition decreased as the amount of deicers increased. The reinforcing steels under the freeze-thaw cycle condition showed the least corrosion, whereas those under the dry-wet cycle condition showed the most severe corrosion /49/.

C. Accumulation of solid corrosion products (oxides/hydroxides) in the concrete pore space near the rebar surface and buildup of tensile hoop stresses around the rebar /50/.

D. Cracking or spalling of the concrete covering the reinforcement.

As a result of this step, moisture, oxygen, and chlorides can gain more direct access to the embedded steel, leaving it more vulnerable to environmental conditions. Therefore, the corrosion rate may be further accelerated /51/.

2.1.2 Comparing Chloride-Based Deicers in Terms of Rebar Corrosion

For practical purposes, all chloride-based deicers were ranked equally high in causing corrosion of the reinforcing steel in a recent NCHRP study, even though hygroscopic chlorides of magnesium and calcium can be more aggressive to the exposed metals than NaCl because of the longer time of wetness /10/. One laboratory study evaluated the corrosivity of various 3% deicer solutions by intermittently spraying them on carbon steel

coupons at room temperature and found that the relative order of deicer corrosivity was as follows from the highest to the lowest: CaCl_2 , MgCl_2 , NaCl , NaCl with a corrosion inhibitor, MgCl_2 with another corrosion inhibitor, CMA, and H_2O /52/.

A study using simulated concrete pore solutions indicated that the corrosion behavior of galvanized steel in the presence of chlorides was controlled by the pH value of the electrolyte, which varies with the cation associated with the chloride anion /53/. MgCl_2 -based deicers applied onto concrete could reduce the pore solution pH (from 12.6 to 9.0 for saturated solutions) by replacing $\text{Ca}(\text{OH})_2$ with $\text{Mg}(\text{OH})_2$, which could result in the loss of iron oxide layer at the rebar surface even in the absence of chloride ions /54/. Therefore, MgCl_2 decreases the threshold chloride level to initiate corrosion and promotes the rebar corrosion /55,56/.

The cation (Na^+ , Ca^{2+} , or Mg^{2+}) associated with Cl^- also affects the chloride diffusion coefficient /20/ and the ranking of diffusion coefficients seem to be independent of the salt concentrations used /10/. In one laboratory study /20/, the chloride diffusion coefficient in Ordinary Portland Cement (OPC) mortar (water-to-cement ratio, $w/c=0.5$) was measured at 9.1 , 22.9 , and $29.0 \times 10^{-12} \text{ m}^2/\text{s}$ respectively for NaCl , CaCl_2 and MgCl_2 at saturated concentrations. In another laboratory study of much more dilute salt solutions /57/, the chloride diffusion coefficient in OPC paste (w/c not specified) was measured at 6.6 , 9.9 , and $20.8 \times 10^{-12} \text{ m}^2/\text{s}$ respectively for NaCl , CaCl_2 and MgCl_2 at 0.5 M concentration. The chloride diffusion coefficients for MgCl_2 are typically two to three times greater than NaCl /20,56,57/, which may significantly reduce the time-to-corrosion-initiation for the rebar in concrete. The effective diffusion coefficient of CaCl_2 was found to fall between that of NaCl and MgCl_2 /20, 57/. It should be noted that temperature variations have a significant

impact on diffusion coefficients and the related transport process, as indicated by a pioneering study by Page et al. /58/. More recent studies by others /59-63/ on concrete or mortar with various w/c ratios suggest that the chloride diffusion coefficient tends to increase with temperature and with w/c values and is also affected by the type of cement used.

2.2 Acetate/Formate-Based Deicer Impacts on Metals

A questionnaire of U.S. airports in 2006 indicated that KAc and sand were most widely used at U.S. airports for snow and ice control of airfield pavements, followed by airside urea, NaAc, sodium formate, propylene glycol-based fluids, ethylene glycol-based fluids, etc. /64/. Acetate-based deicers (KAc, NaAc, and CMA) have also been used on some winter roadways as non-corrosive alternatives to chlorides.

Acetate/formate-based deicers are widely used on airport pavements because they were considered non-corrosive deicer alternatives to chlorides, despite their possible role in accelerating corrosion via some increase in the electrolyte conductivity /10/. It was found that changing from NaCl to an acetate deicer decreased the corrosion rate of steel rebar in a simulated concrete pore solution by more than a factor of ten /65/. Recently, however, potassium formate was reported to cause serious corrosion to landing gear and associated wiring of some Boeing airplane models and the corrosion risk of acetate/formate-based deicers to cadmium-plated steel has raised concerns by aircraft manufacturers and airlines /64/. A recent study in our laboratory revealed that while NaAc- or KAc-based deicers were non-corrosive to mild steel, they were comparably corrosive as chloride-based deicers to galvanized steel /2/.

CMA is generally considered to be less corrosive to metals than NaCl /29/, even though this consensus is mostly based on existing laboratory studies involving the direct exposure of rebar or steel coupons to CMA solutions, which may not represent the case where the rebar is embedded in concrete /10/. Electrochemical and weight loss tests of 14-17 month duration indicated that bridge structural metals, including steel, cast iron, aluminum, and galvanized steel corroded considerably less in CMA solutions than in NaCl solutions /66/. Full and half immersion, vapor space, sprays, and dip testing of ASTM A-36, A-325, and A-588 steel, gray cast iron, and aluminum indicated that CMA solutions were less corrosive to all the metals tested than NaCl solutions /67/. However, similar to NaCl, CMA caused a substantial shift of the potential of steel in mortar, simulated pore solutions, and concrete slabs, indicating the increased risk for steel corrosion /67/. This may be attributed to the fact that CMA reduced the pH of simulated pore solutions, by precipitating OH⁻ ions as Ca(OH)₂ and Mg(OH)₂ /67/. It is noteworthy that in another study, the steel embedded in concrete ponded with CMA solutions did not show any significant potential shifts or corrosion whereas the steel embedded in concrete ponded with NaCl solution did /68/. In CMA solutions of 2 wt.% and higher, reverse polarization scans indicated an unusual electrochemical behavior occurred with three current reversals. It is proposed that carbon dioxide is formed as a consequence of an electrochemical reaction involving the acetate ion. The carbon dioxide then dissolved in the solution, leading to the precipitation of insoluble carbonates at cathodic sites on the steel surface /69/.

Currently there are conflicting data as to whether CMA can be used as an effective corrosion inhibitor for chloride-induced corrosion of reinforcing steel. The ASTM G 109 ponding test results suggested that CMA as an additive to NaCl (in a ratio of 1 to 2) did not

inhibit the rebar corrosion in concrete /70/. One study confirmed that sodium acetate, urea and CMA were only marginally effective as corrosion inhibitors for rebar in concrete, by examining the electrochemical behavior of iron in cured cement pastes /71/. In contrast, another study indicated that adding CMA to a steel-concrete system undergoing active chloride-induced corrosion slowed corrosion after 30 days and stopped corrosion after 60 days /72/. Compared with salt solution made with pure NaCl, a solution made with 20/80 NaCl/CMA mixture (w/w) was 45 percent less corrosive to steel /73/. The impedance and voltammetric measurements confirmed that adding CMA to a simulated pore solution diminished the corrosion rate and increased the protectiveness of surface films /74/.

3. Quantification of Deicer Impacts to Metals

3.1 Common Test Methods of Deicer Corrosivity

The following sections describe common methods for testing deicer corrosivity. Other test methods such as ASTM B117 are not included since they are rarely used for the evaluation or quality assurance of deicer products.

3.1.1 PNS/NACE Test Method

This test method is based on the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the Pacific Northwest Snowfighters (PNS). The test procedure uses 30 ml of a 3% chemical deicer solution per square inch of coupon surface area for the corrosion test /75/. The PNS/NACE test involves a gravimetric method that entails cyclic immersion (10 minutes in the solution followed by 50 minutes exposed to air) of multiple parallel coupons for 72 hours on a custom design machine. The gravimetric method gives the average corrosion rate over a period of time. The weight loss result in

MPY (milli-inch per year) is translated into a percentage, or percent corrosion rate (PCR), in terms of the solution corrosivity relative to a eutectic salt brine.

3.1.2 SAE J2334 Test Method

This test method developed by the Society of Automotive Engineers (SAE) places metal specimens in an enclosed chamber and exposes them to changing climates over time. The test procedure is cyclic in nature, consisting of humid stage, salt application stage, and dry stage; and the number of cycles and test duration can be variable /76/. It has been found that 80 cycles of such accelerated laboratory test corresponded well with five years of outdoor, on-vehicle testing for steel /77/. One challenge in implementing the SAE laboratory test method lies in the need to precisely control the relative humidity of the test environment.

3.1.3 SHRP H-205.7 Test Method

This Strategic Highway Research Program (SHRP) test method covers evaluation of the corrosive effects of deicers on metal substrates through continuous immersion, and is used to evaluate the corrosivity of other aqueous, near neutral pH solutions /78/. The test requires longer exposure time (a few weeks) before weight loss data are collected. This test method is also intended to evaluate the effectiveness of corrosion inhibiting additives to deicing chemicals. One drawback in the SHRP laboratory test method lies in the lack of wet-dry cycles that simulate the field exposure of metals to deicers.

3.1.4 A Proposed Test Method

We consider electrochemical techniques an attractive alternative to the gravimetric methods described above, as they allow rapid determination of corrosion rate of metals and reveal information pertinent to the corrosion mechanism and kinetics /79-81/. In many

practical applications, the use of linear polarization resistance (LPR) is preferred due to its simplicity and LPR testing is referenced in ASTM G 3 (Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing); ASTM G 96 (Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment [Electrical and Electrochemical Methods]); ASTM G 102 (Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements); and ASTM B 117 (Standard Method of Salt-Spray [Fog] Apparatus). However, there are concerns over its validity and reliability when LPR is used to quantify the corrosion rate, as it is prone to measuring errors of the test instrument and other variations. For Tafel polarization, the limitation is that the applied perturbation of large amplitude may lead to significant change in the surface state of electrodes, in the solution composition, or in the controlling corrosion mechanism and kinetics. Shi and Song found that the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) derived from weak polarization curves were useful to predict the PCR value at reasonable accuracies /82/. The electrochemical technique was able to rapidly evaluate the corrosivity of deicer products in the presence and absence of corrosion inhibitors. The authors also suggest the use of multi-electrode array (also known as wire beam electrode) in place of the one-piece working electrode in order to enhance the reliability of the electrochemical test and to allow possible investigation of non-uniform corrosion /83/.

To bring to fruition an electrochemical polarization-based standard test protocol for deicer corrosivity, wet-dry cycles and the control of test environment (temperature, relative humidity, etc.) should be incorporated into the test procedure and weak polarization curves of metal coupons should be periodically measured for deicer products typically used by

maintenance agencies at various concentrations. We envision that there would be a strong correlation between the electrochemical data and the PNS/NACE test results.

3.2 Comparing Test Methods

The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. For instance, in a recent study in our laboratory, the PNS/NACE corrosion test using ASTM C4130 carbon steel coupons suggested that plain MgCl_2 was the least corrosive among five common deicers with the same $[\text{Cl}^-]$ concentration of 0.5M, i.e., NaCl , MgCl_2 , CaCl_2 , $\text{NaCl}+10\text{wt.}\% \text{MgCl}_2$, and $\text{NaCl}+20\text{wt.}\% \text{MgCl}_2$, as shown in Figure 2 /82/. Xi and Xie performed metal coupon testing following the ASTM B117 and the PNS/NACE test methods and also found MgCl_2 to be less corrosive than NaCl to the bare metals tested (stainless steel 410 and 304L, aluminum 2024 and 5086, copper wires, and mild steels) /84/. Nonetheless, the SAE J2334 test results led to the opposite conclusion, as shown in Table 2. The inconsistencies in the test results were attributed to the different moisture conditions and to the different properties of the two salts under high humidity environment. MgCl_2 was found to be more corrosive than NaCl in humid environments (due to its hydrophilic nature and higher viscosity of its solution), and NaCl was found to be more corrosive under immersion and in arid environments /84/.

It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals. For instance, corrosion-inhibited deicer product

must prove to be at least 70% less corrosive than NaCl to be qualified for sale in the PNS states, i.e., with a PCR value of 70 or less. However, not all qualified deicer products reached this goal in the field, as revealed by an evaluation project in the State of Washington. The research project compared the corrosion of steel and aluminum exposed to different roadway or roadside environments, where NaCl, corrosion-inhibited MgCl₂, or corrosion-inhibited CaCl₂ were applied for winter maintenance /85/. Exposure of steel coupons mounted underneath motor vehicles to corrosion-inhibited chemicals consistently resulted in less corrosion than exposure to NaCl. These figures ranged as high as 70 percent less corrosive than NaCl and averaged 43 percent. For steel coupons mounted on guardrail posts, more corrosion was found from the exposure to corrosion-inhibited chemicals than from exposure to NaCl, which may be attributed to the difference in longevity and migration behavior of chlorides and corrosion inhibitors in the field, or to the possible effects of stray currents or galvanic corrosion in the field. Corrosion results for sheet aluminum and cast aluminum were less consistent, likely due to the small weight losses susceptible to experimental errors and interferences. The corrosion patterns were consistent between the two years of evaluation /85/.

4. Countermeasures to Manage Metallic Corrosion due to Deicers

Given the importance of the issue, the authors hereby present a wide range of countermeasures that are currently available to manage metallic corrosion due to deicers. Some of them can be used individually or in combination to mitigate the corrosive effects of deicers.

First of all, there is consensus that the most effective means to address concrete durability can be achieved at the design and materials selection stage by using: 1) adequate concrete cover and 2) high-quality concrete. Increasing the thickness of the concrete cover over the steel rebar can be beneficial /54/, with the increased concrete thickness acting as a barrier to prevent various aggressive species from migrating towards the rebar surface, and therefore increase the time for rebar corrosion to initiate. However, the cover thickness cannot exceed certain limits for mechanical and practical reasons /45/. The water-to-cement ratio can be as important as the concrete cover in controlling chloride-induced corrosion of the reinforcing steel. One laboratory study of rebar-concrete prism specimens exposed to 600-day seawater spray cycles identified the w/c ratio from 0.45 to 0.76 as the dominant factor that controls rebar corrosion, while the Cl^- concentration relative to OH^- of the pore fluid was of the secondary importance /8/. Another study of steel-reinforced concrete cylinders subjected to various laboratory conditions indicated that the rebar in high performance concrete (HPC) specimens ($w/c=0.33$, concrete thickness: 75 mm) performed much better than those in OPC specimens ($w/c=0.6$, concrete thickness: 75 mm) in resisting chloride-induced corrosion /86/.

In addition to an appropriate concrete mix design, permeability-reducing admixtures (e.g., mineral and polymer admixtures) are expected to reduce the risk of rebar corrosion and enhance the concrete durability /87-92/. For instance, the chloride diffusion coefficient for $NaCl$, $CaCl_2$ and $MgCl_2$ at saturated concentrations was significantly reduced to 1.4, 1.5, and $1.8 \times 10^{-12} \text{ m}^2/\text{s}$ respectively in slag-blended cement mortar ($w/c=0.5$), confirming the beneficial effects of mineral admixtures /20/. There are two types of concrete porosity that can affect chloride diffusion: macroporosity due to entrapped or entrained air and

capillary porosity due to the presence of free water. Silica fume and other pozzolans can reduce macroporosity since they make concrete more compact, while decreasing the w/c ratio can reduce capillary porosity /93/. As such, concrete with silica fume or other pozzolans can have diffusion coefficients lower than 10^{-12} m²/s, especially when the water-to-cementitious-materials ratio is lower than 0.4.

Other best practices at this stage include: the addition of corrosion-inhibiting admixtures to fresh concrete /88-89, 94-98/, the surface treatment of steel rebar /99-106/; or the use of alternative reinforcement materials /107-108/. For instance, the use of steel fiber reinforcement in concrete limits the deterioration of concrete, while improving the concrete resistance against damage under severe conditions /109/.

Secondly, the corrosive effects of deicers to rebar in concrete deicers can be mitigated by controlling the ingress and accumulation of deleterious species. Existing research generally agrees that a hydrophobic surface treatment with good quality products (e.g., silanes and siloxanes) helps delay/reduce the ingress of chlorides and moisture into the concrete and thus improves the durability of reinforced concrete structures /110-118/. However, there are conflicting data regarding whether such treatment would benefit existing concrete decks with a relatively high level of chloride contamination in the concrete.

Previous research has indicated that once chloride-induced corrosion of the reinforcing steel is initiated in the concrete structure, the only effective means to stop corrosion are the electrochemical methods such as cathodic protection (CP) and electrochemical chloride extraction (ECE) /119/. CP can stop further corrosion of the reinforcing steel regardless of the chloride content in the concrete, by directly shifting the

steel potential from its natural state (corrosion potential) to a value below the equilibrium potential of steel and thus stopping the anodic dissolution /120/. While measured chloride profiles indicated that little chloride migration occurred at low CP current densities of 0.01 A/m², migration away from the rebar and general chloride depletion in its vicinity were observed at current densities of 0.05 A/m² or higher /121-122/. CP was demonstrated to induce microstructure alternations and some micro-cracking, while effectively retarding corrosion-induced crack initiation and propagation /123/. While both techniques proved to extend the service life of the treated structure, ECE offers more advantages over the use of CP such as the elimination of regular maintenance, as it is a one-time treatment electrically removing Cl⁻ from contaminated concrete while generating beneficial hydroxyl ions (OH⁻) at the rebar /124-127/. While ECE gradually gains acceptance by practitioners as a viable rehabilitation measure, numerous studies have been devoted to examine its efficiency, influential factors, and limitations /128-134/. ECE can alter the chemistry and morphology of the cement paste especially near the steel-concrete interface, leading to Na-rich, Ca-Al-rich, Fe-rich, or Ca-rich crystals and an alkali-silica rich gel at the interface /128-129/ and a higher number of pores with a smaller pore size /131/ in concrete.

Thirdly, the corrosive effects of deicers to rebar in concrete can be mitigated by injecting beneficial species into concrete. Alkanolamines and amines and their salts with organic and inorganic acids have been patented as corrosion inhibitors for surface treatment of chloride-contaminated concrete, often as active ingredients of migrating corrosion inhibitors (MCIs). Such organic inhibitors have been claimed to penetrate rapidly into concrete due to their high vapor pressure under atmospheric conditions, but existing research related to their penetration behavior into concrete has been inconclusive so far,

likely due to the diversity in porosity and chemistry of concretes investigated and test methods used /135-137/. Treatment of corroding reinforced concrete with one MCI product was able to decrease the corrosion rate of rebar corrosion induced by concrete carbonation, both for laboratory conditions and site structures /137/. Another MCI product was able to reduce the corrosion rate only when the initial chloride content was below 0.16 wt.% (by weight of cement, $w/c=0.4$ and 0.6), whereas there was no beneficial effect when the initial chloride content was greater than 0.43 wt.% /138/.

Electrical injection of corrosion inhibitors (EICI) is a relatively new technique that uses a setup similar to ECE to drive inhibitor ions into concrete while at the same time removing Cl^- ions out of concrete. The feasibility of this technique was first demonstrated in late 1980s /124/, when quaternary ammonium and phosphonium corrosion inhibitors were developed specifically for electrical injection into concrete ($w/c=0.5$). The study showed that such inhibitor injection could provide adequate corrosion protection to rebars embedded in chloride-contaminated concrete. Limited studies have been published since the SHRP study, likely due to the high cost of aforementioned corrosion inhibitors. A recent study investigated the electromigration of two organic base corrosion inhibitors, *ethanolamine* (pK_a 9.5) and *guanidine* (pK_a 13.6) /17/. In this EICI process, an electric field was applied between steel embedded in concrete and an external anode, with the cathodic current density galvanostatically controlled in the range of $1\sim 5$ A/m² for 3-14 days. Experiments with the same conditions but without an electric field were also conducted, by applying the corrosion inhibitors to similar saturated concrete surfaces from external electrolyte. The inhibitor concentration profiles indicated that the two inhibitors were effectively injected into carbonated reinforced concretes investigated and their electrical

injection in non-carbonated concrete was far less effective. In carbonated concrete, the inhibitors became concentrated near the embedded steel. In non-carbonated concrete ($w/c = 0.65$, $pH > 13$), guanidine penetration was accelerated to a modest extent by the applied field but a 2-week, $5A/m^2$ treatment did not cause sufficient inhibitor to reach the rebar at a cover depth of 35mm. Ethanolamine penetration in non-carbonated concrete was not significantly enhanced by the electric field. These findings were explained in terms of the influence of the pH of the concrete pore solution on the degree of ionization of the organic bases and hence on their tendencies to migrate and neutralize cathodically-generated hydroxyl ions /139/. In a recent study in our laboratory, we assessed the potential applicability of EICI as a routine electrochemical treatment /140/. Eight organic chemicals were selected for preliminary evaluation in terms of their corrosion inhibition effectiveness for ASTM A588 steel in chloride-containing simulated pore solutions. The best performers (tetrabutylammonium bromide and tetraethylammonium bromide) were then further evaluated for their diffusion coefficient in concrete ($w/c = 0.5$) via a customized electro-migration test. The study identified the selection of corrosion inhibitors as a critical component to the successful implementation of EICI practice as a rehabilitative measure for salt-contaminated concrete. The modeling results indicated that when an appropriate corrosion inhibitor was utilized, it was feasible to electrically inject sufficient amount of inhibitor into salt-contaminated concrete within a reasonable time frame /140/.

Furthermore, the use of an applied electric field has been demonstrated effective to realkalize carbonated concrete /141/, to drive Li^+ into concrete and mitigate ASR /142/, and to inject cations (e.g, Zn^{2+}) to rehabilitate concrete cracks /143/.

Finally, in order to minimize the corrosive effects of deicers to metals in transportation infrastructure, it is important for maintenance agencies to continuously seek non-corrosive deicer alternatives /1/ and optimize the application rates of deicers using advanced technologies such as snowplows equipped with sensors /144/. It should be cautioned that deicer products non-corrosive to one metal might be actually corrosive to other metals /1/ and additives used to inhibit certain metallic corrosion may have little to no inhibition effect on other metals /10/.

5. Conclusions

In cold-climate regions such as the northern U.S. and Canada, the growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment. Chloride ingress, either from marine environments or from chloride-based deicers, is one of the primary forms of environmental attack for reinforced concrete structures. Localized corrosion of rebar may occur when water and oxygen are available at the steel surface and the passive film is jeopardized by a decrease in the pH of concrete pore solution and/or by the presence of enough water-soluble chloride ions. Chloride-based deicers can exacerbate the scaling problem and freeze-thaw damage of concrete. Deicers may also pose detrimental effects on concrete infrastructure through their reactions with the cement paste and thus reduce concrete integrity and strength, which in turn may foster the ingress of moisture, oxygen and other aggressive agents onto the rebar surface and promote the rebar corrosion.

For practical purposes, all chloride-based deicers were ranked equally high in causing corrosion of the reinforcing steel in a recent NCHRP study, even though hygroscopic

chlorides of magnesium and calcium can be more aggressive to the exposed metals than NaCl because of the longer time of wetness. The cation (Na^+ , Ca^{2+} , or Mg^{2+}) associated with Cl^- also affects the pH value of the electrolyte and the chloride diffusion coefficient in concrete and thus poses different levels of corrosion risk to the rebar in concrete.

Acetate/formate-based deicers are widely used on airport pavements because they were considered non-corrosive deicer alternatives to chlorides. A recent study in our laboratory revealed that while NaAc- or KAc-based deicers were non-corrosive to mild steel, they were comparably corrosive as chloride-based deicers to galvanized steel.

We consider electrochemical techniques an attractive alternative to the gravimetric methods commonly used to evaluate deicer corrosivity (PNS/NACE, SAE, and SHRP methods), as they allow rapid determination of corrosion rate of metals and reveal information pertinent to the corrosion mechanism and kinetics.

The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals.

There are many ways to manage the corrosive effects of deicers, such as: selection of high-quality concrete, adequate concrete cover and alternative reinforcement, control of the ingress and accumulation of deleterious species, injection of beneficial species into concrete, and use of non-corrosive deicer alternatives and optimal application rates.

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Figure Captions, and Tables

FIGURE 1. A typical corrosion cell in a salt-contaminated reinforced concrete.

FIGURE 2. Corrosivity of five chloride-based deicers (PNS/NACE test) /82/

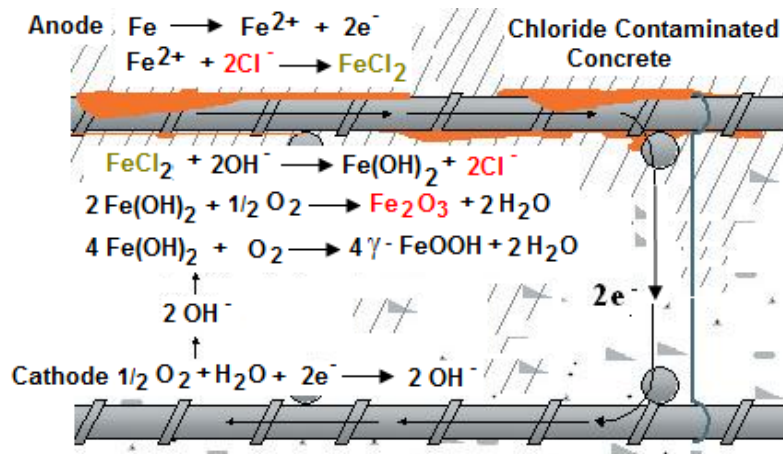


FIGURE 1.

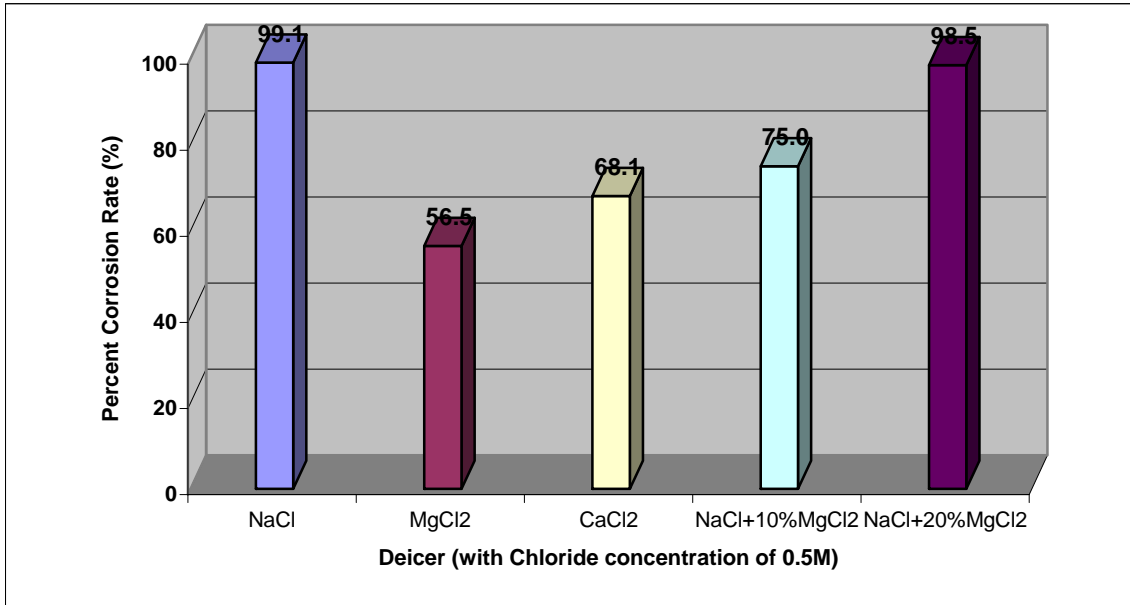


FIGURE 2.

Table 1. Abbreviations and their definitions used in this work.

ASR	Alkali-Silica Reaction
ASTM	American Society for Testing and Materials
C3A	Tricalcium Aluminate
C4AF	Friedel's Salt, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$
CMA	Calcium Magnesium Acetate
CP	Cathodic Protection
C-S-H	Calcium Silica Hydrate
ECE	Electrochemical Chloride Extraction
EICI	Electrochemical Injection of Corrosion Inhibitors
HPC	High Performance Concrete
KAc	Potassium Acetate
LPR	Linear Polarization Resistance
MCI	Migrating Corrosion Inhibitor
MgCl ₂	Magnesium Chloride
MPY	Milli-inch Per Year
NaAc	Sodium Acetate
NACE	National Association of Corrosion Engineers
NCHRP	National Cooperative Highway Research Program
OPC	Ordinary Portland Cement
PCR	Percent Corrosion Rate
PNS	Pacific Northwest Snowfighters
SAE	Society of Automotive Engineers
SHRP	Strategic Highway Research Program

Table 2. A comparison of the corrosion rates obtained by NACE and SAE tests (units given in MPY).

Materials	3 wt.% NaCl solution		3 wt.% MgCl ₂ solution	
	NACE	SAE	NACE	SAE
SS410	1.28	3.71	0.3	19.71
SS304L	0	0	0	0.09
Al2024	0.78	1.39	0.6	4.77
Al5086	No data	0	No data	0.39
A36	No data	77.3	No data	99.8