Corrosion of steel bars in OPC mortar exposed to NaCl, MgCl$_2$ and CaCl$_2$: Macro- and micro-cell corrosion perspective

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ABSTRACT

In North America, corrosion of the steel rebar commonly occurs due to chloride attack from deicing salts. In Canada, based on the severity and temperature of the ambient environment, three different deicing salts, or combination of them, are used: NaCl, MgCl$_2$ and CaCl$_2$. In this paper, the effect of each of these salts on the corrosion of steel rebar and their impact on the durability of the mortar have been investigated. The results show that CaCl$_2$ has the most negative effect on the steel and, in high concentrations, on the integrity of the mortar. MgCl$_2$ also deteriorates the mortar if used in high concentration, while NaCl has no apparent effect on mortar durability even in high concentration.

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1. Introduction

Low cost, readily available raw materials and ease of forming at ambient temperatures make steel reinforced concrete the most widely used structural material. Concrete provides corrosion resistance to the steel reinforcement physically, by acting as a barrier and chemically, due to its high pH where the steel becomes electrochemically passivated. However, reinforcing steel does corrode. The two main causes of reinforcement corrosion are localised breakdown of the passive film on the steel by chloride ions and general breakdown of passivity due to neutralization of the concrete by reaction with atmospheric carbon dioxide. However, chloride-corrosion of steel bars is the most common cause of the degradation of reinforced concrete in North America. When chlorides penetrate concrete, some of them are bound either in the form of Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) or physically adsorbed on the amorphous calcium silicate hydrates (C–S–H) [1]. The remaining "free" chlorides can depassivate the rebar and initiate corrosion on the steel. The source of chloride ions is not important from the point of view of corrosion; nevertheless, the associated cation can affect the corrosion of the steel bars by changing the chemistry of the cement paste and of the pore solution. Consequently, more access of steel to aggressive chloride ions. It is documented that NaCl has little or no effect on the property of concrete, while CaCl$_2$ and MgCl$_2$ can alter the paste chemistry and chemically attack the concrete if they are used in high concentrations [1–4]. This paper addresses macro- and micro-cell corrosion of steel bars in ordinary Portland cement mortar exposed to NaCl, MgCl$_2$ and CaCl$_2$, initially at low concentration and, subsequently, at the maximum concentration used in the field. Macro-cell or galvanic corrosion can occur when the actively corroding bar is coupled to another bar which is passive or has a lower corrosion rate, either because of its different composition or different environment. Micro-cell corrosion is the term given to the situation where active dissolution and the corresponding cathodic half-cell reaction (the reduction of dissolved oxygen) take place at adjacent parts of the same metal part [5].

2. Experimental procedure

Mortar specimens, illustrated in Fig. 1, consisted of a 152 mm × 152 mm × 102 mm (6 in. × 6 in. × 4 in.) mortar prisms containing four 228.6 mm (9 in.) lengths of #5 (6.35 mm or 0.25 in ø) steel reinforcing bars. One bar was positioned at the top with a cover depth of ~9.7 mm (0.375 in.) and three bars at the bottom, with the same cover depth. To prevent extraneous effects, the ends of the bars were coated with epoxy resin to define the exposed length (76.2 mm of the bar within the mortar). Nine specimens, with water:cement: sand ratios of 0.5:1.0:3.0, were cast. Type 10 Portland cement was used in this study.

The specimens were prepared for corrosion measurements as follows: (i) the vertical surfaces were coated with epoxy resin to prevent access of oxygen from those surfaces; (ii) a ponding well was mounted on the top surface; and (iii) the three bottom bars were connected together and then connected to the top bar through a 100 Ω resistor. The ponding well was filled with a salt solution corresponding to a 3% Cl$^-$ (weight percent) concentration for 2-week periods followed by 2 weeks without solution. Three specimens were exposed to each of the salts, NaCl, CaCl$_2$ and MgCl$_2$.

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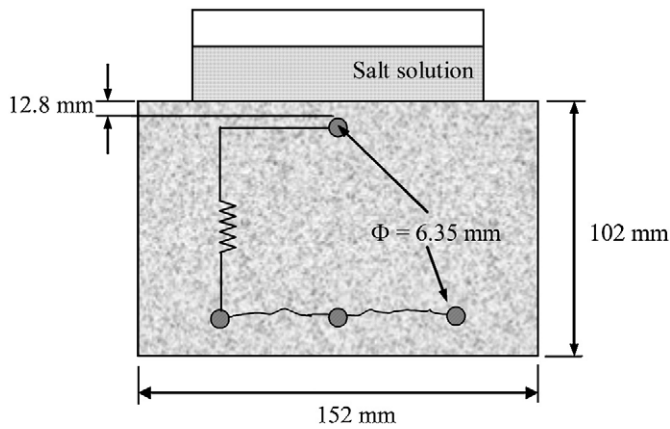E-mail address: poursaee@purdue.edu (A. Poursaee).

Fig. 1. Schematic illustration of the specimens used in this experiment.

The macro-cell corrosion rate, i.e. the current flowing between the bottom bars, in chloride-free mortar, and the top bars, in mortar of increasing chloride content as the salt penetrated the concrete cover, was monitored by measuring the voltage drop across the resistor in after the first week of each two week salt exposure period. The micro-cell corrosion rate of the top bar was determined by the linear polarization resistance (LPR) technique using a saturated calomel reference electrode and a stainless steel counter electrode immersed in the ponding solution. The top bar was disconnected from the bottom bars and the system was allowed to stabilize for 24h before the micro-cell corrosion rate was measured.

After 130 weeks of experiment, some of the samples were autopsied and the surface of the steel bars was visually inspected for the extension of the corrosion products. Fig. 2 shows the surface of the top steel bar in one of the samples exposed to $CaCl_2$. As can be seen, the surface is severely corroded and determining the actual corroded area during the experiment was not possible. Therefore, in all calculations, the whole exposed length of the steel bar (76.2 mm) was used to calculate the surface area and consequently the corrosion current density.

After discussions with several Ontario Municipal officials, it was ascertained that, in some jurisdictions, the deicing salts were being applied as concentrated brines. Therefore, after 31 cycles (124 weeks), the solution concentration was changed to 30% and monitoring continued as before. The experiment was terminated after a further 6 weeks because of excessive deterioration of the prisms exposed to $CaCl_2$.

3. Results and discussion

The micro-cell corrosion current densities of all specimens are given in Fig. 3. For the first ~60 weeks, the bars in all specimens exhibited fairly similar corrosion rates, with those exposed to NaCl exhibiting the highest corrosion rates in the first few weeks and those exposed to $MgCl_2$ being at the lower end of the range.

After this time, the corrosion rates of bars exposed to $CaCl_2$ and NaCl increased by a factor of 2–3 while that of the bars exposed to $MgCl_2$ remained approximately constant.

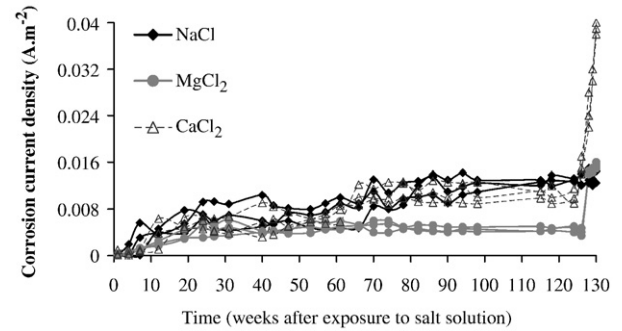**Fig. 2.** Surface of top steel bar in one of the specimens exposed to $CaCl_2$ for 130 weeks.

Fig. 3. Micro-cell corrosion current density as a function of the exposure time to different de-icing salt solutions.

The lack of active corrosion of the bars in $MgCl_2$ is attributed to the precipitation of brucite $(Mg(OH)_2)$ in the pores of the surface layers of the mortar, thereby, limiting the further ingress of chlorides.

When the concentration of the salt solutions was increased to 30%, there was a very rapid increase in the micro-cell current density of the bars exposed to $CaCl_2$ and $MgCl_2$ but those exposed to NaCl showed little change.

The macro-cell current densities are plotted versus time of exposure in Fig. 4. In the first 70 weeks of exposure to 3% salt solutions, active macro-cell corrosion was only observed to be initiated in the specimens exposed to $CaCl_2$. This is indicative of damage to the concrete, permitting easy transport of ions between the top and bottom bars.

The macro-cell current densities are plotted against the micro-cell current densities measured at the same time for the individual specimens with the top bar disconnected from the bottom bars in Fig. 5. For the samples exposed to NaCl and $MgCl_2$ solutions, the micro-cell corrosion rates are higher than the macro-cell corrosion rates and this difference is greater for the specimens exposed to NaCl solution than for those exposed to $MgCl_2$. However, except in the early stages of exposure, the macro- and micro-cell corrosion rate of the samples exposed to $CaCl_2$ are similar. The macro-cell corrosion current densities are higher than micro-cell corrosion current densities at low corrosion rates which could be the result of more ionic resistance in the early ages. However, over the time, the difference between environments (top and bottom parts of the samples) became less significant and the measured values are mostly due to the direct result of corrosion activities on the surface the top rebars.

Macro-cell currents are controlled by the resistance to an ionic current flow in the concrete between the top bar and the bottom bars. On the other hand, for micro-cell corrosion, the anodic and cathodic half-cell reactions can take place at adjacent locations (on a microscopic scale) on the bar and require very short ionic current paths [5]. Therefore, micro-cell corrosion always exists (for both passive and active corrosion) whereas macro-cell corrosion is believed to occur in structures with multiple rebar mats when actively
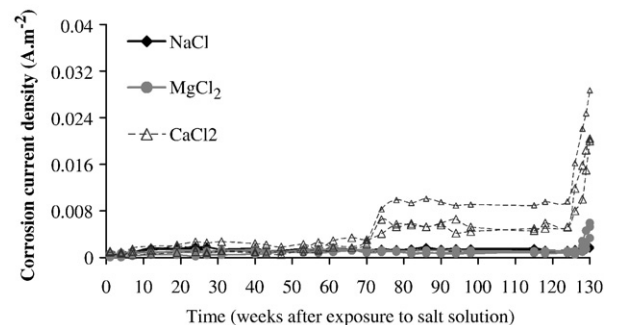

Fig. 4. Macro-cell corrosion current density as a function of the exposure time to different de-icing salt solutions.
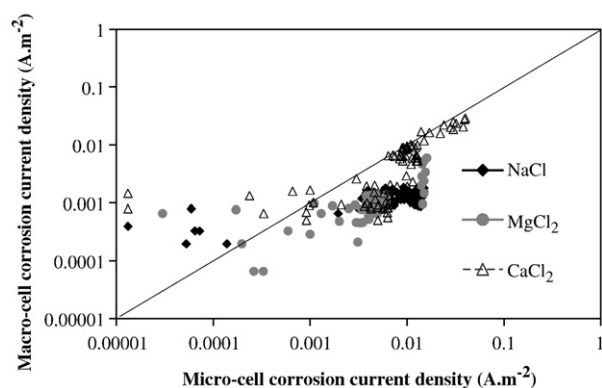
Fig. 5. Comparison between macro- and micro-cell corrosion current densities.

corroding bars are coupled to other bars which are passive or have lower corrosion rates, either because of their different composition or different environment. An example of the former situation is black steel in chloride-contaminated concrete in contact with stainless steel; the latter situation can occur when a top black steel mat in chloride-contaminated concrete is coupled to a bottom black steel mat in chloride-free concrete.

A second factor in the different behaviour is the change in cement paste and pore solution caused by the salts. It is well documented that higher percentage of the chloride is bound when the chloride originated from $CaCl_2$ than when associated with other cations [6–9]. Additions of $CaCl_2$ decrease the pH of the pore solution, and consequently shift the equilibrium which exists between free and bound chloride towards the bound chloride [10]. On the other hand, NaCl increases the pH and, therefore, more free chloride would be available [11]. The sequence of salts with decreased chloride binding capability is as following: $MgCl_2$, $CaCl_2$, KCl and NaCl [6,12–14]. Hansson et al. [7] concluded that $CaCl_2$

has two deleterious effects: in addition to reducing the pH of the pore solution, it also creates a more open pore structure (due to accelerated hydration of the cement) which allows easier diffusion and results in a lower electrical resistivity. NaCl also increase the porosity of the concrete, but to a lesser extent. Therefore, the differences observed in Fig. 5 indicate that specimens exposed to $CaCl_2$ had less ionic resistance than the other specimens and sum of macro- and micro-cell corrosion due to calcium chloride is more significant.

From Figs. 3 and 4, it is clear that by increasing the salt concentration from 3 to 30%, the corrosion current density of the specimens exposed to $CaCl_2$ and $MgCl_2$ increased significantly. This was particularly evident in the case of calcium chloride solution. However, the corrosion current density of the steel in the specimens exposed to NaCl, remained almost the constant. Visual observations, illustrated in Fig. 6, showed extreme deterioration in the specimens exposed to $CaCl_2$ after only six weeks exposure to the high salt concentration; large cracks were created and continued through the mortar to the bottom of the specimens. There was also damage in the specimens exposed to $MgCl_2$ but to a lesser extent and cracks appeared on the top of the specimens but did not propagate through the specimen. However, the surfaces of the specimens exposed to $MgCl_2$ were also softened and "mushy". No significant damage was observed on the samples exposed to NaCl, even after increasing the concentration. Similar results were observed by Darwin et al. [15] by measuring the loss of dynamic modulus of specimens exposed to NaCl, $MgCl_2$ and $CaCl_2$. It was only after exposure to the 30% solutions that this extensive damage was visually observed, but the macro-cell data suggest that damage had already initiated in the specimens exposed to 3% $CaCl_2$ solution.

To identify the cause of such behaviour, XRD analysis was performed on cement powders from the specimens and the results are shown in Fig. 7. These data also indicate that sodium chloride did not induce any detectable change in cement paste. The major cause of deterioration by $MgCl_2$ is believed to be the formation of relatively
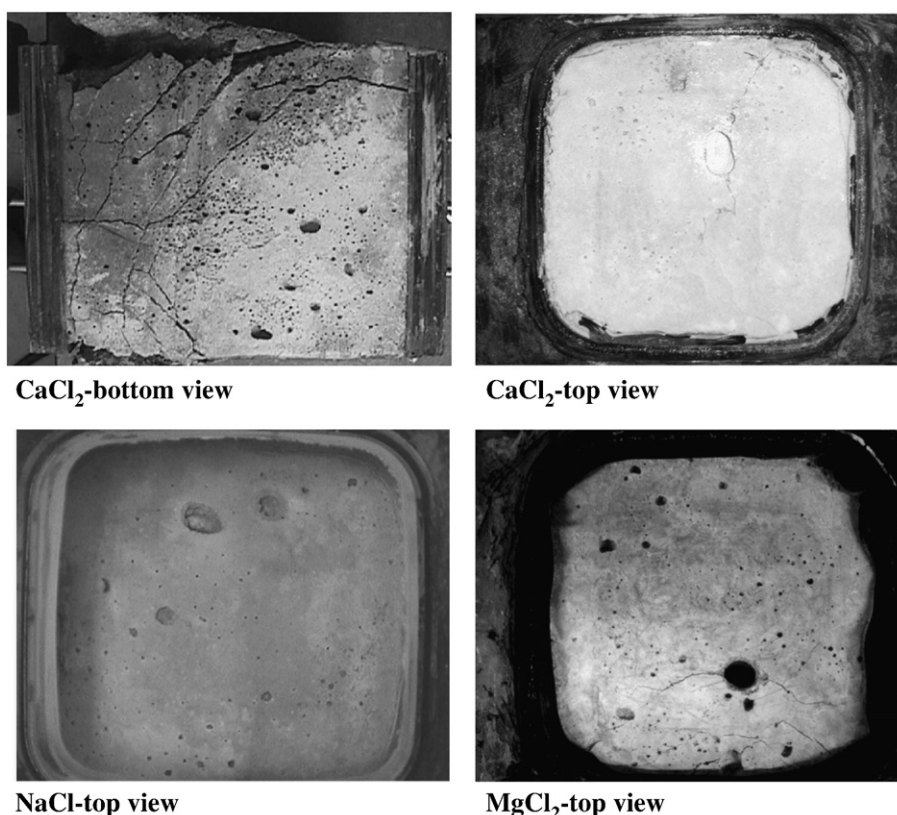

CaCl₂-bottom view

CaCl₂-top view

NaCl-top view

MgCl₂-top view

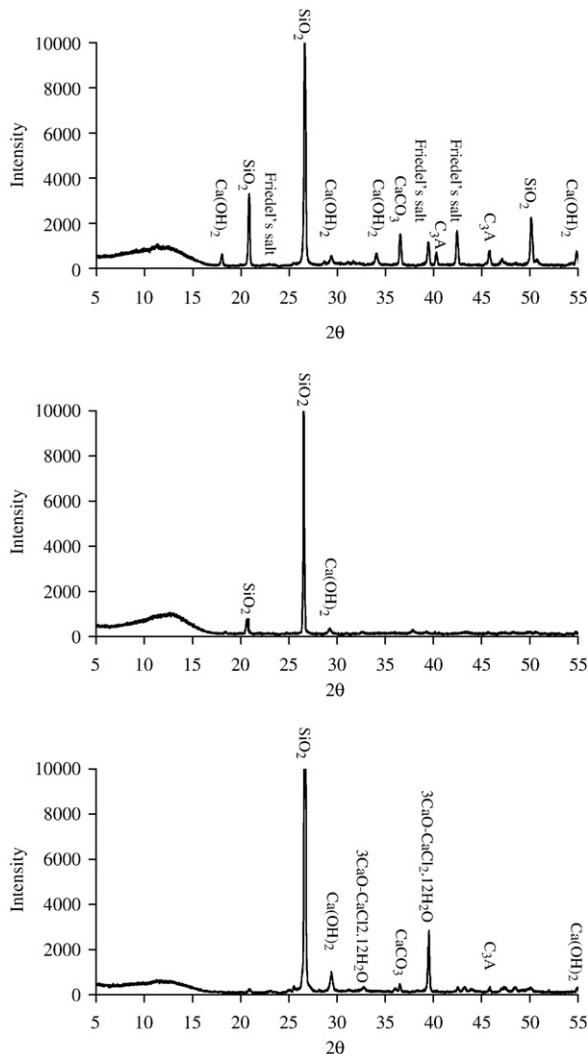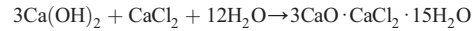**Fig. 6.** Surface of the specimens, 130 weeks after exposure to different salt solutions.

Fig. 7. XRD patterns of mortar powders, gathered from 10 mm below the top surface of the specimens: (a) NaCl, (b) MgCl₂; and (c) CaCl₂.

cited many studies that $3CaO \cdot CaCl_2 \cdot 15H_2O$ is the main form of $3CaO \cdot CaCl_2 \cdot xH_2O$ when concrete is being attacked by $CaCl_2$ according to the following reaction:

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO \cdot CaCl_2 \cdot 15H_2O$$

$3CaO \cdot CaCl_2 \cdot 15H_2O$ is not stable in dry condition and decomposes to $3CaO \cdot CaCl_2 \cdot 12H_2O$ and identifying $3CaO \cdot CaCl_2 \cdot 15H_2O$ in attacked regions is very difficult due to its instability [23,25]. Formation of $3CaO \cdot CaCl_2 \cdot 15H_2O$ damages the concrete matrix because of the hydraulic pressures generated [23]. In addition, leaching of $Ca(OH)_2$ from the matrix leave the porous paste behind which makes the concrete more susceptible to freeze-thaw action [19].

It should be mentioned that the cement powers for XRD analysis were taken from the areas adjacent to the surface of the steel bars and the surface of the specimens exposed to $CaCl_2$ and $MgCl_2$ and very similar results were obtained. Specimens exposed to $CaCl_2$ and $MgCl_2$ were sufficiently cracked to the level of the rebar allowing direct access of the solution. Thus it is reasonable to assume that the chloride concentration in the cracks at rebar was approximately the same as that of the ponding solution, i.e. 30%, which would account for the excessive corrosion shown in Fig. 2.

4. Conclusion

1. Micro-cell corrosion current densities of steel in the specimens exposed to $CaCl_2$ and NaCl solutions are higher than those exposed $MgCl_2$. It is believed that this is due to the formation of brucite in the surface layers of the mortar which fills the pores and reduces further ingress of chlorides.
2. Macro-cell corrosion of the specimens exposed to $CaCl_2$ initiates at an early stage indicative of damage to the mortar allowing easy ionic transport between the top and bottom bars. Moreover, after macro-cell corrosion is initiated, the macro- and micro-cell corrosion rates are very similar.
3. The corrosion behaviour of steel bars in mortar specimens exposed to 3% Cl^- as NaCl and $MgCl_2$ are similar. However, by increasing the solution concentration, corrosion of steel in the specimens exposed to $MgCl_2$ increased, significantly.
4. By increasing the salt concentration from 3% to 30%, severe deterioration was observed in the mortar specimens exposed to $CaCl_2$ and, to a lesser extent, in those exposed to $MgCl_2$. No damage was seen on the specimens exposed to NaCl.

Acknowledgement

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soft phases of magnesium silicate hydrates, M–S–H due to the reaction of dissolved magnesium with calcium silicate hydrates (C–S–H) of the cement [16]. Since the M–S–H has low crystallinity [17], no sharp peak on the XRD pattern appears for M–S–H, as seen in Fig. 7(b). However, as mentioned above, the soft structure of the M–S–H was visually observed on the specimens exposed to magnesium chloride solution and was more obvious after increasing the concentration of the solution. The other possible cause of damage due to MgCl₂ attack is replacement of calcium by magnesium which releases the mobile calcium. This calcium then precipitated as CaCO₃ and/or Ca(OH)₂, or calcium oxychloride or hydroxychloride, whose peaks may overlap those of calcium hydroxide in the cement paste and aggregate pores which may initiate micro-fracturing [2]. However, this cannot be the main reason in the present case, due to relatively weak carbonate peaks on the XRD pattern. It has been shown that the high concentration of CaCl₂ deteriorates concrete [3,18–20]. Hydrated calcium monochloroaluminate ($C_3A \cdot CaCl_2 \cdot xH_2O$) can be identified in calcium chloride attacked cement concrete. It is concluded that $3CaO–CaCl_2 \cdot xH_2O$ is the main cause of damage in the mortar attacked by concentrated CaCl₂ [18,20–24]. Demediuk et al. reported that calcium oxychloride can be formed as $3CaO \cdot CaCl_2 \cdot xH_2O$ where x can vary from 8 to 13 [18]. Brown and Bothe [21] and Shi [3] mentioned that calcium oxychloride can exist as $3CaO \cdot CaCl_2 \cdot 12H_2O$ and it is very unstable and decomposes rapidly. However, M. Collepardi et al. [20]

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