Influence of Associated Cations on Chloride Ingress into Concrete Structures

Nattapong Damrongwiriyanupap¹,a*, Worathep Sae-Long¹,b, Suchart Limkatanyu²,c, and Yunping Xi³,d

¹ Department of Civil Engineering, School of Engineering, University of Phayao, Phayao 56000, Thailand
² Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Songkla 90112, Thailand
³ Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, CO 80309, United States
E-mail: ¹nattapong.d@up.ac.th (Corresponding author), bworathep.sa@up.ac.th, csuchart.l@psu.ac.th, dyunping.xi@colorado.edu

Abstract. This article presents an experimental study on the effect of different types of chloride-based deicing salts on the rate of chloride penetration into concrete structures. Three different types of deicers commonly used for deicing and anti-icing operations, NaCl, CaCl₂, and MgCl₂, were selected to investigate the influence of associated cations on the rate of chloride ingress into concrete. The concentration profiles of various ions were measured including Cl⁻, Na⁺, K⁺, Mg²⁺ and the effect of different cations on the diffusion rate of chloride ion into concrete was systematically studied. The test data were compared to numerical results obtained from a numerical model developed based on the Nernst-Planck equation which considered the ionic coupling effects among ions in chloride solutions and ions in concrete pore solution, Na⁺, K⁺, OH⁻. The test results illustrated that cations in different chloride solutions have significant effects on the penetration rate of chloride ions. This can be summarized in the order of CaCl₂ > NaCl > MgCl₂ from the fastest to slowest chloride ion penetration. In the case of various salt combinations tested, the diffusion rate of chloride ions can be ranked as NaCl + CaCl₂ > CaCl₂ + MgCl₂ > NaCl + MgCl₂. The total chloride concentration obtained from experimental results were compared to the numerical model and a good agreement was observed.

Keywords: Deicing salts, chloride penetration, coupling effect, durability, concrete.
1. Introduction

It is well known that chloride is one of the most significant causes of corrosion of steel in reinforced concrete (RC) structures. This deterioration problem can significantly reduce the load-bearing capacity, service life, and aesthetics of RC structures subjected to chloride environments such as bridge decks, concrete pavements, parking garages, and marine/offshore structures. The degradation due to steel corrosion is a very severe problem for the long-term performance of RC structures. Thus, there is a pressing need to study chloride-induced corrosion of reinforcing bars. Deicing salts are the major sources of chloride ions and they are widely used for ice and snow control on roads and bridges in North America and in the countries with heavy snowfall. In some areas, one mile of four-lane roadways requires the application of more than 100 metric tons of deicing salts each year. About 15.4 million tons of road salts used annually in the U.S. for deicing of highways and roadways [1]. Recently, in 2014, the amount of deicing salts applied on roadways in the U.S. increases up to 17 million tons annually reported by the U.S. Geological Survey [2]. In each year, the U.S. spends $2.3 billion in order to keep roadways clear of snow and ice and it costs $38 million in Colorado reported by Colorado Department of Transportation (CDOT) for an average winter season [3-5]. The American Highway Users Alliance revealed that heavy snowstorm can cost some states $300-$700 million in direct and indirect costs due to lost business income and productivity [6].

The commonly used deicing salts are sodium chloride (NaCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂). Calcium magnesium acetate (CMA), potassium acetate (KAC), sodium acetate (NaAC), and potassium formate (KCHO₂) [1, 7]. However, based on the survey reported by Fay et al. [7], acetates/formates deicers have been used less than 25% while chloride-based deicers are still the most widely used deicing salts. Over the past several years, MgCl₂ liquid deicer has been used by CDOT as an anti-icing chemical applied before a snow storm, because it is more effective, less toxic, and relatively friendly to the environment [8-11]. However, Levelton Consultants Limited [12] and Trahan and Peterson [13] found that MgCl₂ has more harmful effect on infrastructures and roadside vegetation than NaCl so that some local agencies have stopped using MgCl₂ and replaced it by NaCl. In short, several different types of deicing and anti-icing chemicals are used for deicing and anti-icing operations, and the effect of each type of deicer on concrete structures should be studied and understood.

In the actual winter operation of highways and roadways, different deicers are frequently used on the same areas for ice and snow control, for example, magnesium chloride solution can be used before a snow storm for anti-icing, and calcium chloride solid salt can be used during a snow storm for deicing. As a result, multiple species of deicing salts coexist on the surface of roadway and the chemicals penetrate into concrete simultaneously. The review of available literature showed that very few experimental studies were conducted on the simultaneous penetration of different deicing salts into concrete, which is the primary focus of this study. This paper focuses on transport mechanisms of deicing salts into concrete not on scaling and/or damage of concrete due to chloride attack.

Many researches have been contributed on experimental study of chloride ingress into concrete that the studies were conducted by mixing and/or immersing cement paste specimens or mortars with different types of chloride solutions. Different from those studies, concrete specimens were ponded on the top surface by different types of solutions made of various chloride-based salts that can represent the use of deicers in the reality. This method is similar to the test of AASHTO T 259 (Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration). The penetration rates of the chloride as well as positive ions were studied and analyzed. The penetration processes were considered as one-dimensional rather than two-dimensional diffusion which is the case of concrete samples immersed in chloride solutions.

Al-Hussaini et al. [14] conducted an experimental study on the effect of free chloride ion source mixed in cement mortar. Two different types of chlorides, NaCl and CaCl₂, were used in the study. They found that NaCl presented more free chloride ion than CaCl₂ at all concentrations, from 0.5% to 2% by mass of cement, and pH of cement mortars were lower in the case of NaCl. As a result, cement mortars mixed with NaCl can accelerate the corrosion mechanism when compared with CaCl₂. On the other hand, Arya et al. [15] reported that CaCl₂ had greater effect than NaCl in terms of producing more free and bound chloride ions when mixed in concrete and immersed in the chloride solutions. Also, they found from the thin cement paste specimens immersed in 20 g/l of different types of chloride solutions that associated cation in the chloride solutions was one of the most important factors affecting chloride binding capacity. The highest free chloride content was found from the specimens immersed in MgCl₂ solution and it decreased in the order of MgCl₂ > NaCl > Sea-water > CaCl₂. The same trend was also seen in the case of bound and total chloride that samples submerged in MgCl₂ had the highest binding chloride and total chloride content, and it could be ranked in the order of MgCl₂ > CaCl₂ > NaCl > Sea-water for both bound and total chloride content.

The penetration rate of different types of deicing salts in concrete was selected as the indicator in this study for the penetration of chloride driven by more than one type of deicers. The difference in the penetration rate of different deicers is caused by associated cations in the chloride solutions. The laboratory tests were conducted to evaluate the penetration rates of six different groups of chloride-based deicers, i.e. 3% NaCl, 3% CaCl₂, 3% MgCl₂, 3% NaCl + 3% CaCl₂, 3% NaCl + 3% CaCl₂, and 3% CaCl₂ + 3% MgCl₂. The ponding test was used in the study. This method was chosen because it is very much similar...
to the actual situation in reality, where deicing salts are applied on the top surface of concrete structures such as pavements, parking lots, and bridge decks, and then ingress into the deep portion of concrete where reinforcing steels were located.

2. Experimental Procedure

The mix proportions with two different water-cement ratios, 0.55 and 0.65, were used in this study, shown in Table 1. Portland cement type I was used in the concrete mixtures. The fine aggregate was the local river sand with a specific gravity of 2.65 and a fineness modulus of 2.50, while coarse aggregate was the crushed lime stone with the size of 19 mm and a specific gravity of 2.70, respectively. After 28 days of curing, all specimens were immersed in water for 30 days to achieve saturation. The chloride ponding test was conducted in saturated condition and in room temperature at 20°C so that the effects of moisture and temperature can be excluded. The average 28-day compressive strengths of the concrete samples for w/c = 0.65 and 0.55 are 22.06 and 24.43 MPa, respectively. In order to perform chloride ponding test, the ponding reservoirs were designed and installed on top of concrete specimens. The reservoirs were made by 5" (12.5 cm) tall plastic sleeves cut from PVC concrete cylinder molds with 4" (10 cm) diameter. Then, PVC sleeves were put on the top of concrete specimens for 2" (5 cm) in depth that created a 3" (7.5 cm) reservoir on the top surface of specimens. Steel band clamps were used to tighten the PVC sleeves. A bead of silicone was added around the interface between sleeve and specimen to further prevent water leakage and create watertight compartment for chloride solution at the top of specimen as seen in Fig. 1.

Table 1. Concrete mix design.

<table>
<thead>
<tr>
<th>Content</th>
<th>Proportions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mix 1</td>
</tr>
<tr>
<td>Water-cement ratio (w/c)</td>
<td>0.65</td>
</tr>
<tr>
<td>Weight of water (kg/m³)</td>
<td>232</td>
</tr>
<tr>
<td>Weight of cement (kg/m³)</td>
<td>356</td>
</tr>
<tr>
<td>Weight of sand (kg/m³)</td>
<td>847</td>
</tr>
<tr>
<td>Weight of gravel (kg/m³)</td>
<td>904</td>
</tr>
</tbody>
</table>

Once the silicone had dried, all specimens were exposed to chloride solutions. The six different groups of chloride solutions, as mentioned above, were ponded on the top of samples. The bottom face of specimen was exposed to distilled water and kept in room temperature as shown in Fig. 2. The experimental program is summarized in Fig. 3. After each exposure period (15 and 30 days) the samples were removed from the solutions and cleaned by removing salts, and then dried at room temperature for one day. After the specimens had dried the surface were cleaned from salt deposit on the top surface by using a wire brush. In order to obtain chloride profiles, the chloride concentrations at different depths were measured by samples of concrete powder collected at various depth from the surface exposed to chloride solutions by the water-soluble method [16]. The results from this analysis represented in a profile of free chloride concentration as a weight percentage of concrete weight [17]. The concentration of sodium and potassium ions was analyzed using titration method.

3. Results and Discussion

The free chloride concentration profiles corresponding to different types of deicing salts are illustrated in Figs. 4-11. Figures 4, 5, 8, and 9 are plotted for specimens with 0.55 w/c exposed to the chloride solutions, and Figs. 6, 7, 10 and 11 represent the samples with w/c = 0.65. These plots show both 15 and 30 days of exposure and will be discussed in three cases; 1) chloride profiles of samples exposed to different single types of salts (3% NaCl, 3% CaCl₂, and 3% MgCl₂); 2) different combinations of the salts (3% NaCl + 3% CaCl₂, 3% NaCl + 3% CaCl₂, and 3% CaCl₂ + 3% MgCl₂); and 3) the effect of cations. In the discussion of the three cases, the test data will also be compared with simulation models.

Fig. 1. A concrete specimen prepared for the chloride ponding test.

Fig. 2. Chloride ponding test set up.
### 3.1. Case 1: Single Salt Ponding

It can be observed from the profiles in Fig. 4, 5, 8, and 9 that the chloride concentration decreases with increasing depth from the top surface and the chloride concentrations from 3% CaCl$_2$ solution tend to be the highest when compared to 3% NaCl and 3% MgCl$_2$ at the same depth. This is because 3% solid CaCl$_2$ salt diluted in water produces more chloride ions than 3% NaCl and 3% MgCl$_2$. The generation of the three chloride-based salts in solution can be described as Eq. (1), (2), and (3). In order to compare the test results with numerical results, 3% NaCl, 3% CaCl$_2$, and 3% MgCl$_2$ by weight diluted in 1 liter of distilled water can be converted into mol/l as 0.513, 0.270, and 0.148, respectively. One can see from Eq. (1) through (3) that 3% CaCl$_2$ can generate chloride ions higher than 3% NaCl and 3% MgCl$_2$, and 3% MgCl$_2$ produces the smallest amount of chloride ions in solution. This means, at the fixed depth, the highest chloride concentration is found in the case of 3% CaCl$_2$ and the lowest one occurs in the case of MgCl$_2$.

\[
3\% \text{NaCl} \rightarrow Na^+ + Cl^- \\
(0.513 \text{ mol/l}) + (0.513 \text{ mol/l})
\]  

(1)

\[
3\% \text{CaCl}_2 \rightarrow Ca^{2+} + 2Cl^- \\
(0.270 \text{ mol/l}) + 2(0.270 \text{ mol/l})
\]  

(2)

\[
3\% \text{MgCl}_2 \rightarrow Mg^{2+} + 2Cl^- \\
(0.148 \text{ mol/l}) + 2(0.148 \text{ mol/l})
\]  

(3)

However, there is a slight difference of chloride concentration that can be observed in the cases of 3% CaCl$_2$ and 3% NaCl. This is because these two salts produce almost the same amount of chloride ions. Another reason is due to the use of low alkali cement and low concentration of chloride solutions. This can be explained by the Nernst-Planck equation as illustrated in Eq. (7) and will be discussed later that the ionic interaction among ions in chloride solutions and ions in concrete pore solution. So, the rate of chloride penetration under single salt ponding mainly depends on the amount of chloride in the solution. The other ions (positive or negative ions), such as Na$^+$, K$^+$ and OH$^-$, have less effect on the penetration rate of chloride [18-25].

![Fig. 3. Summarization of experimental study program.](image)

![Fig. 4. Chloride profiles of concrete specimen at 15 days of exposure with 0.55 water-cement ratio.](image)

![Fig. 5. Chloride profiles of concrete specimen at 30 days of exposure with 0.55 water-cement ratio.](image)

![Fig. 6. Chloride profiles of concrete specimen at 15 days of exposure with 0.65 water-cement ratio.](image)
3.2. Case 2: Multiple Salts Ponding

As previously mentioned, in reality, more than one type of deicing salts are frequently used at the same location on pavements and parking structures. Therefore, how different types of salts contribute to the penetration mechanism of chloride in concrete is important. To this end, the three groups of mixed chloride solutions were ponded on the top of concrete specimens. The chloride profiles at 15 and 30 days of exposure are shown in Fig. 8 and 9 for the concrete samples with 0.55 water-cement ratio and Figs. 10 and 11 for the samples with 0.65 water-cement ratio.

Similar to the experimental results of single type of salt, the specimens exposed to the combinations of CaCl₂ with another type of salt tend to have higher concentration at the same depth, which correspond to the faster rate of chloride penetration. The highest concentration is found in the case of 3% NaCl + 3% CaCl₂ which provides the highest concentration of chloride ions in the solution as noticed in Eq. (4). The specimens exposed to 3% NaCl + 3% MgCl₂ and 3% CaCl₂ + 3% MgCl₂ have lower chloride concentrations than that of 3% NaCl + 3% CaCl₂ due to the lower concentrations of chloride ions in the solutions as shown in Eq. (5) and (6).

$$\text{3% NaCl} + \frac{3}{2}\text{CaCl}_2 \rightarrow \text{Na}^+ + \text{Ca}^{2+} + 3\text{Cl}^-$$

$$\text{0.513 mol/l} + \frac{0.270}{2}\text{mol/l} \rightarrow \text{0.513 mol/l} + \frac{0.270}{3}\text{mol/l} + \frac{1.053}{3}\text{mol/l}$$

(4)

$$\text{3% NaCl} + \frac{3}{2}\text{MgCl}_2 \rightarrow \text{Na}^+ + \text{Mg}^{2+} + 3\text{Cl}^-$$

$$\text{0.513 mol/l} + \frac{0.148}{2}\text{mol/l} \rightarrow \text{0.513 mol/l} + \frac{0.148}{3}\text{mol/l} + \frac{0.809}{3}\text{mol/l}$$

(5)

$$\text{3% CaCl}_2 + \frac{3}{2}\text{MgCl}_2 \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{Cl}^-$$

$$\text{0.270 mol/l} + \frac{0.148}{2}\text{mol/l} \rightarrow \text{0.270 mol/l} + \frac{0.148}{4}\text{mol/l} + \frac{0.836}{4}\text{mol/l}$$

(6)

The transport process of multiple ionic species in concrete can be described using Nernst-Planck equation which includes two transport mechanisms due to the concentration gradient and the ionic interaction. The flux equation of each ionic species is expressed as:

$$J_i = -D_i \left( \frac{\partial C_i}{\partial x} + \frac{z_i F \partial \phi}{RT} C_i \right)$$

(7)

where $C_i$ is the ion concentration, $D_i$ is the diffusion coefficient, $z_i$ is the charge number, $F$ is the Faraday’s constant, $R$ is the gas constant, $T$ is the temperature, $\Phi$ is the electrostatic potential, and index $i$ represents the $i$-th species.
Theoretically, the Nernst-Planck equation can be used to explain the penetration of multi-types of chloride solutions into concrete. The equation takes into account the ionic coupling among ions in solutions and ions in concrete pore solution, \( K^+, Na^+ \), and \( OH^- \) [18-25]. This is necessary because different type of salt has different associated cation that can affect the ionic transport, and the effect is taken into account mainly in the second term of Eq. (7). In order to compare the experimental results with theoretical prediction based on the Nernst-Planck equation, the test results of concrete specimens exposed to chloride solutions with 0.55 water-cement ratio at 15 and 30 days of exposure are plotted against the numerical results obtained by the Nernst-Planck equation [17]. Figures 12 through 15 show the total chloride profiles obtained from the present study compared to the numerical results. It is evident that the concretes subjected to 3% MgCl\(_2\) have lower chloride concentration than 3% NaCl and 3% CaCl\(_2\) at 15 and 30 days of exposure as shown in Figs. 12 and 13, respectively. While, chloride concentrations in specimens exposed to 3% NaCl are quite similar to 3% CaCl\(_2\) at any depths. This is due to 3% NaCl solution provides amount of chloride ions almost equivalent to 3% CaCl\(_2\) solution which is 0.513 mol/l and 0.540 mol/l for 3% NaCl and 3% CaCl\(_2\), respectively, whereas, chloride ions released from 3% MgCl\(_2\) are lower than that of 3% NaCl and 3% CaCl\(_2\) as explained in Eq. (1) through (3). Similar tendencies are observed for the specimens exposed to 3% MgCl\(_2\) mixed with other two chloride solutions, 3% NaCl and 3% CaCl\(_2\). As exhibited in Figs. 14 and 15, chloride ions produced from 3% MgCl\(_2\)+3% NaCl and 3% MgCl\(_2\)+3% CaCl\(_2\) are less than 3% NaCl+3% CaCl\(_2\) resulting in lower chloride concentrations at 15 and 30 days of exposure. In addition, chloride concentrations in concrete ponded with 3% MgCl\(_2\)+3% NaCl are almost the same as 3% MgCl\(_2\)+3% CaCl\(_2\) at any depths. This can be clearly explained as Eq. (4) through (6) that the mixed chloride solution of 3% MgCl\(_2\)+3% NaCl produces the amount of chloride ions (0.809 mol/l), which is almost equivalent to the solution of 3% MgCl\(_2\)+3% CaCl\(_2\) (0.836 mol/l) and chloride ions created from each of these two mixed solutions is less than the solution of 3% NaCl+3% CaCl\(_2\).
concentration is from the top surface (the exposed surface) to the bottom surface so the magnesium concentration decreases when the depth increases. From the comparison point of view, it can be concluded that the cations in the chloride solutions have influence to a certain extent on the penetration of chloride ions into concrete structures.

4. Conclusions

1) An experimental study was conducted on the penetration of various types of deicing salts into concrete. Three different types of deicers, i.e. chloride-based salts, were selected to investigate the penetration rate of chloride solutions.

2) Concrete specimens were divided into six groups exposed to six different chloride solutions: three single salt solutions 3% NaCl, 3% CaCl₂, 3% MgCl₂; and three multi-salt solutions 3% NaCl + 3% CaCl₂, 3% NaCl + 3% MgCl₂, and 3% CaCl₂ + 3% MgCl₂.

3) In order to investigate the penetration mechanisms of the multispecies chloride solutions, the moisture and temperature effects were excluded by using saturated and isothermal condition.

4) The experimental results show that the chloride penetration rate depends on the chloride concentration generated by the deicing chemicals, and that the cations in chloride solutions have significant effect on the penetration rate of chloride ions. The chloride penetration rates of the chemicals can be summarized in the order of CaCl₂ > NaCl > MgCl₂ from the fastest to slowest chloride ion penetration in the case of single salt solutions. In the case of multi-salt combinations, the penetration rate of chloride ions can be ranked as NaCl + CaCl₂ > CaCl₂ + MgCl₂ > NaCl + MgCl₂.

5) The corrosion initiation time of reinforcing steel in reinforced concrete structures exposed to different deicers can vary due to the critical chloride content contributed from salts which produce various levels of free and bound chloride ions. From the present experimental results, the deicing salts with CaCl₂ can produce the highest penetration rate for chloride ions.

6) The experimental results are compared to the numerical results obtained based on the Nernst-Planck equation which accounts for the interaction between multiple ions. A good agreement was obtained in terms of total chloride concentration. The monotonic trends of sodium, potassium, and magnesium profiles obtained from the experiment is noticed when compared to the mathematical model.
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References


**Dr. Nattapon Damrongwiriyanupap** is currently an Associate Professor in Department of Civil Engineering, School of Engineering, University of Phayao, Thailand. He received his PhD in Structural Engineering and Structural Mechanics (SESM) from the University of Colorado, Boulder, USA.

His research interests focus on computational modeling of multi-physics transport in concrete, green concrete structures for sustainability, and reutilization of various solid wastes in concrete structures.

**Dr. Worahep Sae-Long** was born in Hat-Yai, Songkhla, Thailand in 1989. He received the B.S. degree in civil engineering from the Prince of Songkla University, Songkhla, Thailand in 2012 and the M.S. and Ph.D. degrees in structural engineering from Prince of Songkla University, Songkhla, Thailand, in 2019.

His research interests include soil structure interaction, numerical simulation, mathematical modelling, nanostructure systems, nonlinear analysis, and seismic analysis.

**Dr. Suchart Limkatanyu** is Professor in the Department of Civil Engineering at Prince of Songkla University, Thailand. He received his PhD in Structural Engineering and Structural Mechanics (SESM) from the University of Colorado, Boulder.

His research interests focus on the seismic analysis, design and retrofitting of reinforced concrete structures, earthquake engineering, computational mechanics, nonlinear frame analysis, nano-engineering and technology, and multi-physics systems.

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Dr. Yunping Xi is a Professor of Structural Mechanics and Structural Engineering in Department of Civil, Environmental and Architectural Engineering at the University of Colorado, Boulder, USA. He received his PhD in Structural Engineering from Northwestern University.

His research interests include theoretical analysis and experimental study on long term durability of cementitious materials and reinforced concrete structures, monitoring and simulation of long-term performance of reinforced concrete and steel structures, evaluation of existing nuclear power plant structures: containment structures, bioshieldings, and dry casks, and development of sustainable construction materials for the earth and space construction.