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## **PHYSICAL AND CHEMICAL EFFECTS OF DEICERS ON CONCRETE PAVEMENT: LITERATURE REVIEW**

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## LIST OF ACRONYMS

ACR	alkali-carbonate reaction
ASR	alkali-silica reaction
C-N(K)-S-H	calcium alkali silicate hydrate
C-S-H	calcium silicate hydrate
CH	calcium hydroxide
CMA	calcium magnesium acetate
M-S-H	magnesium silicate hydrate
N(K)-S-H	alkali silicate hydrate

## **EXECUTIVE SUMMARY**

The purpose of this research was to conduct a thorough review of the literature and summarize the effects of several commonly used deicers on concrete pavement. Sodium chloride, calcium chloride, magnesium chloride, and calcium magnesium acetate (CMA) and the effects of their respective ions are specifically discussed, and 10 different studies published between 1995 and 2012 that were performed to compare the effects of various deicers are summarized.

Deicers can affect concrete both physically and chemically. Physical effects are typically manifested as cracking and salt scaling. Several mechanisms have been proposed to explain the phenomenon of salt scaling, including thermal shock, precipitation and growth of salt crystals, osmotic pressure, and glue spalling. Chemical effects can result from reactions involving cement hydration products, aggregates, or reinforcing steel. Reactions caused by deicer ions include the leaching of calcium hydroxide from the paste, the decalcification of calcium silicate hydrate (C-S-H), the conversion of C-S-H to magnesium silicate hydrate (M-S-H), and the formation of brucite, complex salts, and oxychlorides. The alkali-silica reaction and alkali-carbonate reaction can be initiated and accelerated by alkalis from deicers. Accumulation of critical concentrations of chloride ions in the vicinity of the steel can initiate corrosion.

Most strategies used by researchers to directly compare the effects of various deicers on concrete involve freeze-thaw cycling, wet-dry cycling, and/or soaking mortar or concrete specimens. Regardless of variations in testing methods and specimen characteristics, the results from nine of the ten studies summarized in this research indicate that specimens exposed to sodium chloride experienced only minor, if any, adverse effects, while specimens exposed to calcium chloride, magnesium chloride, or CMA experienced significant deterioration, including scaling, cracking, mass loss, and compressive strength loss. The researchers found that the deterioration suffered by specimens exposed to calcium chloride was caused by the formation of calcium oxychloride and complex salts, while specimens exposed to magnesium chloride and CMA deteriorated because of M-S-H and brucite formation.

Given the results of this literature review, engineers responsible for winter maintenance of concrete pavements should utilize sodium chloride whenever possible, instead of calcium chloride, magnesium chloride, or CMA, and apply only the amount that is absolutely necessary to ensure the safety of the traveling public. In addition, when new winter maintenance treatments are considered, the chemical composition of the treatments should be carefully evaluated with respect to the potential damage that may be caused to the pavement.

## **1.0 INTRODUCTION**

### **1.1 Problem Statement**

Winter weather affects 70 percent of the roadways in the United States each year (1), with snow and ice often compromising roadway safety, highway capacity, and economic stability. In order to maintain serviceability throughout the winter months, several methods are used to remove snow and ice from roads, one of which is the application of anti-icing and deicing chemicals. Anti-icers are applied before a storm to prevent the formation of a bond between ice and the pavement surface, while deicers are applied after ice has formed in order to melt and break down the ice. The primary purpose of both techniques is to aid the removal of snow and ice with snow plows.

Unfortunately, anti-icers and deicers (hereafter referred to collectively as deicers) often have negative impacts on the pavement. Deicers affect asphalt pavement negligibly but can cause significant problems on concrete pavement (2). Deicers affect concrete both physically and chemically. The physical effects of deicers on concrete are mainly manifested in increased damage from freeze-thaw cycling, while the chemical effects include detrimental reactions between the deicers and the cement paste, aggravation of expansive aggregate-cement reactions, and initiation and acceleration of corrosion when reinforcing steel is present in the concrete. Damage from deicer exposure can be manifested as surface scaling, cracking, concrete degradation, delamination, and premature failure.

Because deicers can reduce the service life of a concrete pavement, they can have potentially significant hidden costs. Possible damaging effects need to be considered along with other factors such as service temperature, environmental effects, and price when selecting deicers for application especially on concrete pavements. The purpose of this research was to conduct a thorough review of the literature and summarize the effects of several commonly used deicers on concrete pavement. Sodium chloride, calcium chloride, magnesium chloride, and calcium magnesium acetate (CMA) and the effects of their respective ions are specifically discussed.

While other deicing chemicals such as urea and sodium formate are also available, they are used primarily on airport runways and are beyond the scope of the present work.

## **1.2 Concrete Properties**

Concrete is comprised of aggregates bound together by a portland cement paste that hardens through hydration reactions. The principal products of these reactions are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). C-S-H occupies over 50 percent of the volume of normal cement pastes and is the primary source of concrete strength. CH constitutes 20 to 25 percent of the paste volume. It fills many of the pores in the paste and therefore contributes a degree of strength to the concrete (3). While largely inert, C-S-H and CH are susceptible to attack from certain chemicals, some of which are found in deicers.

Being a porous material, concrete is filled with small voids known as capillary pores, which range in size from  $2.0 \times 10^{-4}$  mils (5 nm) to  $3.9 \times 10^{-2}$  mils (1  $\mu\text{m}$ ); concrete designed for use in cold regions also frequently contains entrained air bubbles, which range in size from 0.39 mils (10  $\mu\text{m}$ ) to 3.9 mils (100  $\mu\text{m}$ ) (4). These pores are often filled with a solution of water and chemicals to which the concrete has been exposed, with the degree of pore saturation depending on the environmental conditions. This pore structure allows chemicals to penetrate the concrete and makes the concrete susceptible to freeze-thaw damage.

## **1.3 Report Outline**

This report contains four chapters. Chapter 1 presents the objectives and scope of the research. In Chapter 2, the mechanisms through which deicers damage concrete are discussed. Reviews of the pertinent laboratory studies performed to compare the effects of selected deicers are presented in Chapter 3. In Chapter 4, the research findings are summarized, and recommendations are given.

## **2.0 DETERIORATION MECHANISMS**

### **2.1 Overview**

Deicers damage concrete through a combination of physical and chemical effects. The physical effects are the same for all deicers, while the chemical effects depend on the chemical composition of the deicers, as described in the following sections.

### **2.2 Physical Effects**

Most concrete deterioration induced by deicers is principally a result of physical processes. This damage is typically manifested in cracking and salt scaling, as shown in Figure 2-1. Scaling by itself will not incapacitate a concrete pavement, but it leads to greater concrete saturation and ingress of aggressive chemicals that may be present in the environment, making the concrete more susceptible to frost action and chemical attack. Several mechanisms have been proposed to explain the phenomenon of salt scaling, including thermal shock, precipitation and growth of salt crystals, osmotic pressure, and glue spalling.

Thermal shock occurs in the concrete when deicers are applied to the concrete surface. When deicers are applied to ice, the melting point of the ice is reduced. If the melting point is reduced to a temperature lower than the temperature of the ice, the ice begins to melt. The requisite energy for melting is drawn from the concrete surface, which causes rapid cooling of the concrete surface. A temperature gradient is quickly formed that results in differential strain within the concrete. The concrete surface then experiences tensile stress (5), which may cause small cracks in the concrete that result in scaling of the concrete surface.



**Figure 2-1 Salt scaling.**

The formation and growth of salt crystals in concrete pores can generate significant tensile stress in the concrete surface (5, 6, 7). Following deicer application, the concentration of salt ions at the surface of the concrete generally exceeds the concentration of salt ions within the pores of the concrete, causing a downward diffusion of salt ions into the concrete. As the concrete dries during periods of low precipitation and/or low humidity, the concentration of salt ions in the pore solution increases due to the evaporation of water from the pores. Salt then begins precipitating from the solution to form crystals within the pores (8, 9); this crystal growth has been shown to be capable of producing tensile hoop stresses above 2,500 psi (17.2 MPa) (10).

Over time, dissolved deicing chemicals can become concentrated in pores within the concrete. The large concentration affects the osmotic pressure that develops in the concrete during freezing. When the pore water freezes, salt ions are excluded from the ice and are then concentrated in the remaining pore water in a supercooled state. The development of these localized high ion concentrations creates concentration gradients in the pore water system, which in turn cause water molecules in areas of lower concentration to diffuse towards areas of higher

concentration. The osmotic pressure resulting from this water diffusion creates tensile stresses in the concrete, especially near the surface where salt concentrations are high. Osmotic pressure may be a viable explanation for salt scaling (11).

Some researchers, noting the similarities between scaled concrete and scalloped glass, have suggested a mechanism similar to glue spalling as a primary cause of salt scaling (12). Glue spalling is a technique that is used to create shallow scallops in decorative glass. It is performed by spreading a layer of epoxy over the glass surface at high temperature and then allowing the composite to cool. Because the coefficient of thermal expansion for epoxy is higher than that of glass, the contraction from cooling is significantly greater in the epoxy than in the glass. The epoxy eventually breaks into small islands, which create tensile stress in the glass at the island edges. The cracks spread and eventually form small scallops on the glass surface. When ice forms on a concrete surface and temperatures continue to drop, the ice and concrete may behave like an epoxy/glass composite. Cooling temperatures cause ice to contract as much as five times more than concrete. Glue spalling also accounts for the fact that low chloride concentrations always produce the most salt scaling. Researchers have observed that salt scaling is most extreme when chloride concentrations are between 2 and 4 percent, regardless of the type of deicer used (13). Glue spalling explains this pessimum concentration because the freezing behavior of ice is dependent on the concentration of deicing chemicals in the solution. At salt concentrations lower than 2 percent, ice contracts at a rate similar to concrete as temperatures decrease, which prevents the ice from generating stresses in the surface of the concrete. On the other side of the pessimum, as salt concentrations increase beyond 4 percent, the ice does not develop enough strength to crack concrete.

Thus, as has been documented in this section, several mechanisms have been proposed to explain the physical effects of deicing salts on concrete. However, no specific mechanism has yet been found to be solely responsible for salt scaling. Damage may be caused by just one mechanism or by the combined effects of several. While researchers have diverse views on these mechanisms, they are in agreement that the best ways to minimize the physical effects of deicers are air entrainment and proper finishing techniques (4).

## 2.3 Chemical Effects

The chemical effects of deicers are often overshadowed by the physical effects, but they can be significant nonetheless. While the severity and type of reaction may vary, each of the deicers considered in this research chemically reacts with concrete in some way (14). Reactions may involve cement hydration products, aggregates, or reinforcing steel. Ion-paste reactions, aggregate cement reactions, and corrosion are described in the following sections.

### 2.2.1 Ion-Paste Reactions

Ions contained in deicers often react with cement paste in ways that are harmful to concrete. In this section, reactions caused by deicer ions, including the leaching of CH from the paste, the decalcification of C-S-H, the conversion of C-S-H to magnesium silicate hydrate (M-S-H), and the formation of brucite, complex salts, and oxychlorides, are each discussed.

Several researchers have found that CH is leached from paste by chloride, calcium, and magnesium ions (15, 16, 17, 18, 19). CH is one of the principal products of cement hydration. As stated previously, it usually occupies 20 to 25 percent of the cement paste volume (3). Carde et al. have shown that the effects of CH leaching are significant (20), as the process leads to an increase in concrete porosity (21, 22). In addition to allowing harmful chemicals to penetrate concrete more easily, increased porosity reduces the strength of concrete (17, 23). The effect of chloride ions on CH is consistent, whether the chloride comes from sodium chloride, calcium chloride, or magnesium chloride salts (19). Regarding calcium and magnesium ions, Santagata and Collepari soaked concrete specimens for eight months in a commercial CMA-based deicer and a blend of pure calcium and magnesium acetates (24). They found that exposure to the CMA solutions led to load capacity reduction, mass loss, and visible deterioration. Because replacing portland cement with a slag cement in the concrete reduced the effects of the CMA on the specimens, they concluded that the aggression of CMA is also associated with leaching of CH from the paste.

Chloride ions can also alter the composition of C-S-H in cement paste by removing calcium ions (25, 26). Because C-S-H comprises more than 50 percent of the volume of cement

paste and is the primary source of concrete strength and durability (3), this decalcification process, which increases the microporosity of the concrete, leads to a reduction in concrete strength; however, the effects of C-S-H decalcification are minor when compared to the effects of CH leaching (20, 21, 22).

Magnesium ions cause more severe concrete deterioration than any other constituent of common deicing chemicals (27). This deterioration occurs as a result of a reaction between the magnesium ions and C-S-H. Magnesium reacts with the C-S-H present in cement paste to produce M-S-H (17, 26, 28, 29). Unlike C-S-H, M-S-H is not cementitious; it provides no strength to the concrete. Frigione and Sersale percolated solutions of magnesium chloride through mortar specimens made from various types of cement and found that the magnesium chloride exposure reduced the compressive strength of the mortar between 25 and 40 percent, regardless of cement type. They concluded that the replacement of C-S-H by M-S-H was the cause of the strength reduction (16). Cody et al. also determined, through a series of freeze-thaw and wet-dry experiments, that the major mechanism by which magnesium ions deteriorate concrete is formation of M-S-H (30). Lee et al. found that the replacement of C-S-H by M-S-H resulted in the debonding of fine aggregate from the paste (31, 32).

An additional mechanism by which magnesium ions damage concrete is the formation of brucite ( $\text{Mg}(\text{OH})_2$ ) (18, 26). Brucite crystals are formed in concrete when magnesium ions react with CH. The growth of brucite within concrete pores likely causes crystal growth pressures that lead to concrete expansion (33, 34). This reaction contributes to the damage done to concrete by M-S-H formation (30).

Exposure of concrete to chemicals containing calcium ions can also lead to deterioration (35). Like magnesium ions, calcium ions can lead to destructive crystal growth pressures in concrete (36). Calcium ions react with cement hydration products to form complex salts composed of  $\text{CaCl}_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{CaCO}_3$  (15). Much like brucite, these complex salts form crystals within concrete that create tensile stresses in the concrete.

The principle mechanism through which calcium ions attack concrete may be oxychloride formation. Oxychloride is formed from  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$ , and water. The reaction occurs fastest at temperatures just above freezing, which pavements in cold regions frequently experience during winter. Researchers have found oxychloride, which generates destructive hydraulic pressures in concrete, through petrographic analysis of concrete specimens exposed to  $\text{CaCl}_2$  (34). Monosi and Collepardi have suggested that, while the damage done to concrete by oxychloride formation is typically masked by freeze-thaw damage and damage from corrosion, oxychloride formation leads to considerable concrete degradation (37). They based their conclusions on an experiment in which non-air-entrained mortar specimens were submerged in 30 percent  $\text{CaCl}_2$  solution for two months. The specimens experienced a significant loss in compressive strength, even without freezing temperatures or steel present in the concrete to corrode. An additional study performed by Sutter et al. found that magnesium ion exposure can exacerbate oxychloride formation in concrete (38). They placed mortar cylinders in 15 percent  $\text{MgCl}_2$  for 84 days. Using optical microscopy, scanning electron microscopy, and microanalysis, they were able to identify oxychloride in the exposed specimens. The oxychloride formation was facilitated by  $\text{CaCl}_2$  produced as a byproduct of the conversion of C-S-H to M-S-H by the magnesium ions.

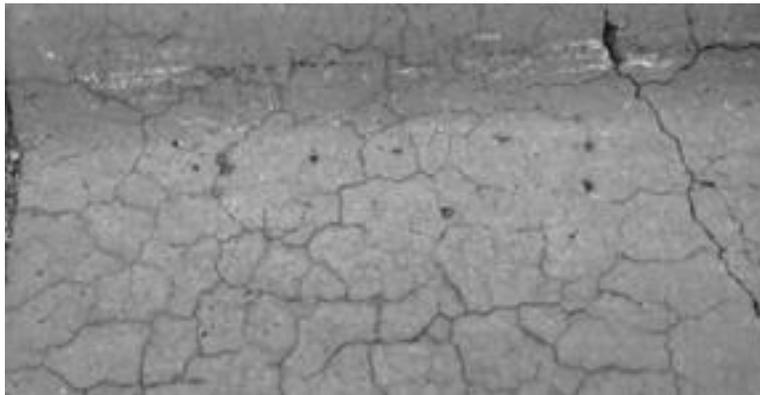
### 2.2.2 Aggregate Cement Reactions

The alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR) can occur in concrete when alkalis from the paste react with certain aggregates. These reactions are expansive and can lead to failure of the concrete. In this section, these reactions and the ways that deicers can affect them are discussed.

ASR occurs in concrete produced with aggregate containing reactive silica. While opal and chert are common forms of reactive silica, other forms of silica have been found to be reactive to a lesser degree. Alkalis and calcium ions from cement present in the pore solution penetrate into reactive aggregate and form a non-swelling calcium alkali silicate hydrate (C-N(K)-S-H) gel, which behaves much like C-S-H, on the surface of the aggregate. The C-N(K)-S-H gel is relatively porous and allows additional alkalis and calcium ions to diffuse into the

aggregate. If the concentration of alkalis is high enough, an alkali silicate hydrate (N(K)-S-H) gel forms because the solubility of CH, the source of calcium ions, is inversely proportional to the alkali concentration. The N(K)-S-H gel diffuses away from the aggregate, where it swells as it attracts water through osmosis. Swelling of the N(K)-S-H gel subsequently produces tensile stresses in the concrete and eventually causes map cracking, as shown in Figure 2-2. As the silica reacts with the penetrating ions, the aggregates become susceptible to further penetration and subsequent reaction (39), and the reaction then occurs at varying speeds depending on the reactivity of the silica, the availability of alkalis, and the amount of moisture present. It has caused concrete failures in time periods ranging from 1 to 50 years (3).

Many researchers have found that deicing salts accelerate ASR in concrete containing reactive aggregate (40, 41, 42, 43, 44, 45). The reaction can be accelerated by any deicer that provides additional alkalis to react with the silica (46). The surplus of alkalis in the pore solution lowers the CH solubility, which increases the formation of swelling N(K)-S-H gel. Researchers have also found that chloride ions from deicing salts can play a role in accelerating ASR (47, 48).



**Figure 2-2 Map cracking caused by ASR (3).**

ACR has been found to occur in concrete with dolomitic aggregate. The dolomite present in the aggregate reacts with alkalis from the cement paste to produce brucite and calcite. The reaction results in a volume increase and subsequent concrete deterioration (3). It also releases magnesium, which can participate in many of the deleterious reactions previously discussed, from the aggregates into the paste (33). Researchers have observed that calcium chloride and sodium chloride can produce the reaction in concrete containing reactive aggregate (33, 49).

### 2.2.3 Corrosion

When reinforcing steel is placed in concrete, the steel is protected from corrosion by a passive oxide film on the surface of the steel. Reinforcing steel does not corrode unless this oxide film is broken down. Because this film is susceptible to chloride ions, accumulation of critical concentrations of chloride ions in the vicinity of the steel can initiate corrosion. In addition to reducing the cross-sectional area of the steel, corrosion produces large tensile stresses in the concrete because the corrosion products are two to six times greater in volume than the parent steel (50, 51). Therefore, rusting of the reinforcing steel leads to delamination of the concrete. The concentration of chloride ions required to initiate corrosion depends on the pH of the pore solution in contact with the steel but is typically between 1 and 2 lb Cl/yd<sup>3</sup> (0.6 and 1.2 kg/m<sup>3</sup>) of concrete (3).

All deicing salts that contain chloride can cause corrosion, but the type of cation paired with the chloride can have a significant effect on the severity of the corrosion by altering the pH of the concrete pore solution. Reductions in the pH of the pore solution reduce the amount of chloride needed to initiate corrosion. Calcium chloride reduces the pH of the pore solution more than other deicing salts because calcium is already present in excess in the cement paste. Any added calcium precipitates out of the pore solution as CH, which removes hydroxyl ions from the solution and therefore reduces the pH. Sodium hydroxide, on the other hand, is highly soluble in the pore solution, so sodium ions introduced through the addition of sodium chloride do not reduce the pH of the pore solution (52). In fact, sodium chloride can actually have the opposite

effect; it can react with calcium aluminate hydrate to produce Friedel's salt and sodium hydroxide, which increases the pH of the pore solution instead (53).

Because calcium chloride and magnesium chloride have a negative effect on concrete durability, they also lead to more corrosion than sodium chloride in reinforced concrete. As the concrete breaks down, the chemicals penetrate the concrete more easily. Poursaei et al. investigated the impact of various deicers in ponding tests on reinforced mortar specimens. They found that calcium chloride and magnesium chloride had a much more negative effect than sodium chloride on the corrosion of the embedded steel (54).

## **2.4 Summary**

Deicers can affect concrete both physically and chemically. Physical effects are typically manifested as cracking and salt scaling. Several mechanisms have been proposed to explain the phenomenon of salt scaling, including thermal shock, precipitation and growth of salt crystals, osmotic pressure, and glue spalling.

The chemical effects of deicers are often overshadowed by the physical effects, but they can be significant nonetheless. Reactions may involve cement hydration products, aggregates, or reinforcing steel. Reactions caused by deicer ions include the leaching of CH from the paste, the decalcification of C-S-H, the conversion of C-S-H to M-S-H, and the formation of brucite, complex salts, and oxychlorides. ASR and ACR can be initiated and accelerated by alkalis from deicers. Accumulation of critical concentrations of chloride ions in the vicinity of the steel can initiate corrosion.

## **3.0 COMPARATIVE LABORATORY STUDIES**

### **3.1 Overview**

Researchers have performed numerous studies to directly compare the effects of various deicers on concrete. Many strategies have been used to simulate the environmental conditions experienced by concrete pavements. Most strategies involve freeze-thaw cycling, wet-dry cycling, and/or soaking of mortar or concrete specimens. Freeze-thaw cycling tends to magnify the physical effects of the deicers investigated, while wet-dry cycling and soaking allow chemical effects to be investigated without the effects of frost action masking the results.

In this chapter, all of the studies known to the authors that have been performed to compare the effects of various deicers are summarized. Ten different comparative studies published between 1995 and 2012 are presented. The procedures, which are crucial to properly interpreting the results, and the conclusions of each study are summarized and reviewed.

### **3.2 Studies**

The studies in this section are presented in chronological order by date of publication. A summary of the methods utilized in each study and the effects of sodium chloride, calcium chloride, magnesium chloride, and CMA, which are the deicers investigated in a majority of the laboratory studies, are presented in Table 3-1.

**Table 3-1 Summary of the Effects of Common Deicers**

Study	Method	NaCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>	CMA
Peterson 1995	Soak	minor	-	-	significant
Cody et al. 1996	F/T, W/D, Soak	minor	significant	significant	-
Lee et al. 2000	F/T, W/D	minor	significant	significant	significant
Sutter et al. 2006	Soak	minor	significant	significant	-
Wang, Nelson, and Nixon 2006	F/T, W/D	minor	significant	-	-
Darwin et al. 2008	W/D	minor	significant	significant	significant
Poursae, Laurent, and Hansson 2010	W/D	minor	significant	significant	-
Shi et al. 2010	F/T	significant	-	minor	minor
Shi et al. 2011	Soak	minor	significant	significant	-
Jain et al. 2012	F/T, W/D, Soak	minor	significant	significant	-

### 3.2.1 Peterson 1995

Peterson performed soak experiments to compare the effects of CMA at two different calcium/magnesium molar ratios with the effects of sodium chloride and calcium acetate on mortar prisms (55). He soaked mortar prisms with water-cement ratios of 0.45 and 0.60 in both saturated solutions and solutions diluted so that their freezing point depression matched that of a 3 percent solution of sodium chloride. For each solution, a test was performed on specimens at 41°F (5°C) and at 68°F (20°C). The specimens were soaked for up to 22 months. In order to establish the effects of the solutions on the mortar specimens, changes in length and mass of each specimen were measured each month. Additionally, compression and flexural strength of the specimens were measured once the immersion period was completed.

Peterson found that, like other solutions containing magnesium, the CMA dissolved the hardened cement paste in the mortar specimens. While the lower saturation reduced the deterioration rate, each of the specimens that were soaked in the CMA solutions experienced significant mass loss, as well as expansion. Additionally, the flexural and compressive strengths of the prisms soaked in the CMA solutions were strongly reduced as a result of the deicer exposure. The calcium/magnesium molar ratio of the solutions did have some effect on the performance of the mortar prisms, as the solutions that had a greater amount of magnesium ions

were more detrimental to the specimens. Peterson suggested that the strength reductions were largely attributable to brucite formation. The sodium chloride solutions had little influence on the length or mass of the mortar prisms and only a minor effect on the compressive and flexural strengths.

### 3.2.2 Cody et al. 1996

In 1996, Cody et al. performed wet-dry, freeze-thaw, and continuous soak experiments on concrete specimens (30). In order to determine the role of concrete quality on the deicer effects, experiments were performed on concrete specimens from pavements classified as durable or non-durable. Concrete pavements with a service life of 40 or more years were classified as durable, while concrete pavements with a service life of 15 years or less before serious deterioration developed were classified as non-durable.

Four-inch cores were taken from highway pavements, and small blocks were cut from the cores. The experiments were performed in 0.75M and 3M solutions of magnesium chloride, calcium chloride, and sodium chloride, along with distilled water, which was used to establish a baseline condition. A few of the experiments were also performed with magnesium acetate and magnesium nitrate in order to determine the effects of anion type on concrete deterioration.

In the wet-dry experiments, concrete blocks were immersed in 140°F (60°C) solutions for 132 hours, followed by a drying period of 24 hours at 140°F (60°C). The specimens were then air cooled to 77°F (25°C), immersed in 77°F (25°C) solutions, and heated in those solutions to 140°F (60°C) to begin another cycle. The high temperatures were chosen to simulate conditions experienced by concrete pavements during hot and dry summers. The short cycling time was used to accelerate test results. Cycling was performed until additional deterioration would prevent petrographic examination of the specimens.

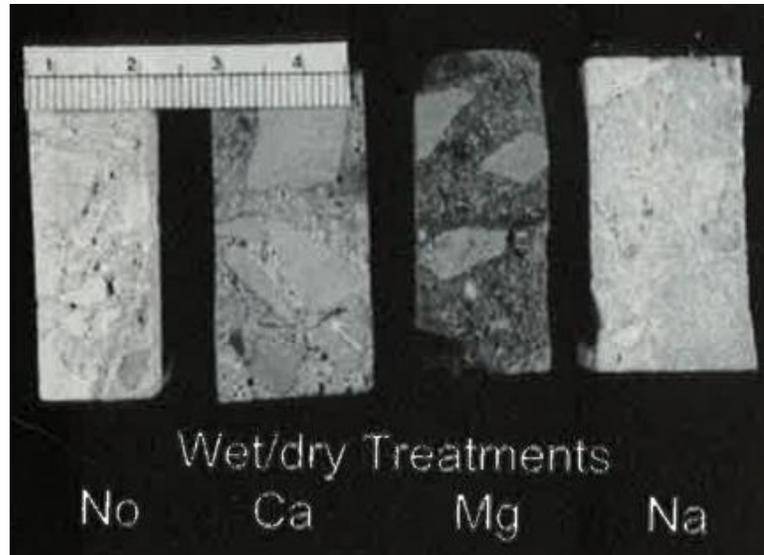
Specimens subjected to freeze-thaw experiments were soaked in 140°F (60°C) solutions for 132 hours, air cooled to 77°F (25°C), frozen at either 24.8°F (-4°C) or -94°F (-70°C) for 24 hours, air warmed to 77°F (25°C), immersed in 77°F (25°C) solutions, and heated in those

solutions to 140°F (60°C) to begin another cycle. The 24.8°F (-4°C) freezing temperature was used in one set of experiments to simulate conditions experienced in the field, while the -94°F (-70°C) freezing temperature was used in the other set in order to completely freeze all of the solutions, which varied in freezing temperature depending on composition.

Continuous soak experiments were performed by constantly immersing concrete blocks in sealed containers at 140°F (60°C). The soaking was terminated at 222 days.

In each of their experiments, the researchers found that calcium chloride and magnesium chloride solutions damaged the concrete measurably, while sodium chloride solutions had only minor effects on the concrete as shown in Figure 3-1. They also found that the effects of magnesium acetate and magnesium nitrate solutions were similar to those of magnesium chloride, suggesting that solutions containing magnesium deteriorate concrete similarly, regardless of the accompanying anion.

The researchers found that M-S-H conversion, as well as brucite formation, led to the deterioration of the magnesium chloride-soaked specimens. They also concluded that formation of complex salts may have been the cause of deterioration in the calcium chloride-soaked specimens. While recognizing that physical effects can accentuate the chemical effects of deicer solutions on concrete, the researchers concluded that chemical effects were the primary cause of the concrete deterioration, even in specimens subjected to freeze-thaw cycling.



**Figure 3-1 Results of wet-dry experiment conducted by Cody et al. (30).**

### 3.2.3 Lee et al. 2000

Lee et al. performed a study to investigate the effects of sodium chloride, calcium chloride, magnesium chloride, CMA at five different calcium/magnesium ratios, calcium acetate, and magnesium acetate (32). Wet-dry and freeze-thaw cycling were used to simulate environmental conditions.

Specimens for the testing were created by cutting small 1.18 x 0.59 x 0.59 in. (3 x 1.5 x 1.5 cm) blocks from cores of seven different highway concretes. Two blocks from each core were placed in each investigated deicer solution. The solutions included sodium chloride, calcium chloride, magnesium chloride, calcium acetate, magnesium acetate, and CMA with a calcium/magnesium ratio of 3:7. Additional experiments were performed using CMA with calcium/magnesium ratios of 7:3, 5:3, 1:1, 3:5, and 7:3. Each of the solutions used had a concentration of 0.75M.

The specimens subjected to wet-dry cycling were immersed in their solutions for 132 hours at 136.4°F (58°C), dried at 136.4°F (58°C) for 24 hours, air cooled to 77°F (25°C),

immersed in 77°F (25°C) solutions, and heated in those solutions to 136.4°F (58°C) to begin another cycle. For freeze-thaw cycling, the specimens were immersed in their solutions for 132 hours at 136.4°F (58°C), air cooled to 77°F (25°C), and stored for 24 hours at 24.8°F (-4°C). The specimens were then air warmed to 77°F (25°C), immersed in 77°F (25°C) solutions, and heated in those solutions to 136.4°F (58°C) to begin another cycle.

Specimens were subjected to the wet-dry or freeze-thaw cycling until they showed visible signs of deterioration, at which point they were cut into thin slices that were used for petrographic analysis. Scanning electron microscopy and energy dispersive analytical X-ray area mapping were used to identify the reactions that had occurred in the specimens during testing.

CMA was the most deleterious of the deicer solutions. All of the specimens exposed to CMA showed visible deterioration after 15 cycles. Twenty-three cycles were required for the magnesium chloride-exposed specimens to show deterioration, while the calcium chloride-exposed specimens showed deterioration between 33 and 49 cycles. Sodium chloride was the least destructive to the concrete.

The researchers identified M-S-H formation as the primary cause of deterioration in the specimens exposed to the CMA solutions. Severe shrinkage cracks developed in these specimens, particularly under the wet-dry conditions. The conversion of C-S-H to M-S-H was especially severe along the boundaries between the fine aggregate and the cement paste and resulted in the fine aggregate becoming debonded from the paste. Some brucite formation also occurred. Similar reactions occurred in the specimens exposed to the magnesium acetate solution. The calcium acetate solution produced the least damage among the acetate solutions.

The calcium chloride solution affected the concrete specimens by causing the formation of calcium oxychlorides within the concrete. Magnesium chloride led to the replacement of C-S-H by M-S-H and the formation of brucite. Abundant shrinkage cracks also developed in the specimens exposed to magnesium chloride. All of the chloride solutions caused paste deterioration by decalcification. Leaching of CH also occurred in each of the specimens exposed to chloride solutions.

### 3.2.4 Sutter et al. 2006

Sutter et al. soaked mortar specimens of various water-cement ratios in concentrated solutions of several deicing chemicals to investigate the detrimental chemical effects of deicers on concrete (34). The tests were performed on mortar specimens with water-cement ratios of 0.40, 0.50, and 0.60.

While the researchers initially performed experiments using three different temperature regimes for up to 84 days, only one yielded significant results. They found that cycling the submerged specimens between 20-hour periods of -15°F (-26.1°C) and 135°F (57.2°C) was ineffective and yielded inconclusive results. They also found that soaking the specimens at a constant temperature of 135°F (57.2°C) led to only minimal concrete deterioration. The temperature regime that provided distinguishing results was a constant 40°F (4.4°C), which is a condition commonly experienced by saturated concrete during winter months.

Solutions of magnesium chloride, calcium chloride, and sodium chloride were used in the study. A concentration of 15 percent magnesium chloride was selected to be similar to the diluted concentration experienced by pavements when salt solutions are applied to a wet road surface. Solutions of 17.0 percent calcium chloride and 17.8 percent sodium chloride were then selected in order to maintain an equal number of moles of each deicer cation per volume of solution for all three types of deicers, allowing a comparison based solely on chemical interaction. Petrographic analysis was performed on specimens at prescribed intervals in order to identify the chemical reactions that were occurring.

The cylinders immersed in the magnesium chloride and calcium chloride solutions first showed signs of cracking and expansion after 56 days of exposure. At the end of the 84-day testing period, these cylinders had severely deteriorated. The damage occurred irrespective of water-cement ratio; however, no damage was sustained by any of the cylinders soaked in the sodium chloride solution.

Using petrographic analysis, the researchers identified calcium oxychloride formation as the primary cause of damage to the specimens. They also found that brucite formation had contributed to the damage of the specimens submerged in the magnesium chloride solution.

### 3.2.5 Wang, Nelsen, and Nixon 2006

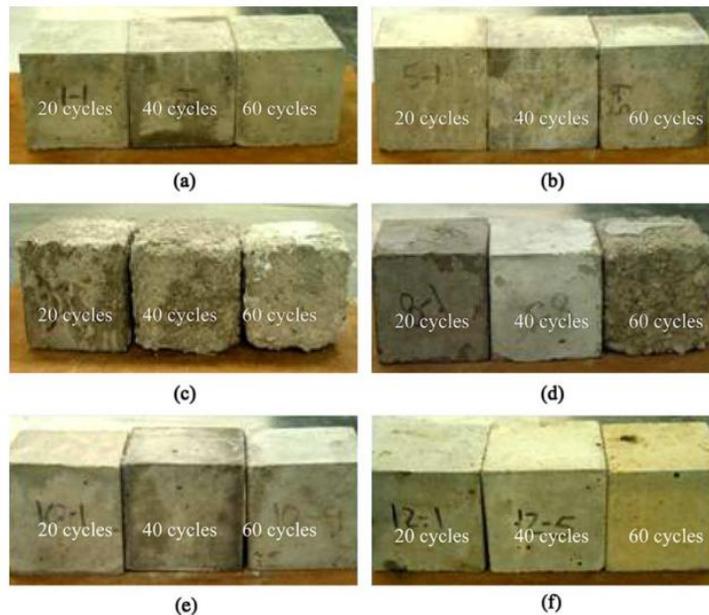
Wang, Nelsen, and Nixon also performed freeze-thaw and wet-dry tests on concrete specimens (19). They measured mass loss, scaling, compressive strength loss, chemical penetration, and changes in micro-structure caused by sodium chloride, calcium chloride, calcium chloride with a reinforcing steel corrosion inhibitor, potassium acetate, and an agricultural product. For the testing, they created both paste and concrete specimens with an air content of 6 percent. The paste specimens had a water-cement ratio of 0.40, while the concrete specimens had a higher water-to-cement ratio of 0.48 to encourage scaling in a shorter time period.

The wet-dry experiments were performed with solution concentrations ranging from 26.5 to 54.5 percent. The range in concentrations was used by the researchers in order to simulate actual exposure conditions under the assumption that users typically apply deicing chemicals directly to concrete pavements at the concentration received from the supplier rather than dilute them. The high concentrations also maximized the potential chemical interactions between the deicers and the paste or concrete. The freeze-thaw experiments were performed with solution concentrations ranging from 9.5 to 13.6 percent. The lower concentrations allowed the paste and concrete specimens to freeze under the freeze-thaw conditions used by the researchers.

The wet-dry regimen used by the researchers involved immersing the specimens in deicer solution at 40°F (4.4°C) for 15 hours and then allowing them to air dry at 73.4°F (23°C) and 50 percent relative humidity for 9 hours. One complete cycle took 24 hours. For freeze-thaw cycling, the researchers immersed specimens in deicer solution, stored the immersed specimens at -4°F (-20°C) for 15 hours, and then thawed them at 73.4°F (23°C) for 9 hours, with a complete cycle also taking 24 hours.

Mass loss, scaling, and compressive strength of the specimens were measured throughout the wet-dry and freeze-thaw regiments. Ion penetration, X-ray diffraction, and scanning electron microscope tests were also performed on the specimens. Testing on each specimen was stopped after 60 cycles were completed.

The researchers found that the calcium chloride solutions, both with and without corrosion inhibitor, caused the most damage to the concrete and paste specimens. The physical conditions of the concrete specimens following testing are shown in Figure 3-2. The specimens exposed to calcium chloride experienced significant mass and compressive strength loss. The damage was caused by the formation of complex salts, CH leaching, and physical stresses caused by the precipitation of salt within the concrete pores. The sodium chloride, potassium acetate, and agricultural deicing product did not cause significant strength or mass loss in the specimens exposed to them. Results were similar for both the paste and concrete specimens.



**Figure 3-2 Specimens exposed to deicers and freeze-thaw cycling: (a) H<sub>2</sub>O, (b) NaCl, (c) CaCl<sub>2</sub>, (d) CaCl<sub>2</sub> with corrosion inhibitor, (e) K acetate, (f) agricultural deicing product (19).**

### 3.2.6 Darwin et al. 2008

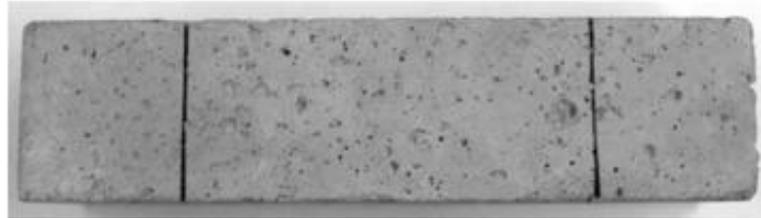
Darwin et al. exposed concrete specimens to week-long wet-dry cycles in sodium chloride, calcium chloride, magnesium chloride, and CMA (56). The testing was performed using two concentrations for each deicer solution, 3 percent and 15 percent by mass. The specimens were tested through the week-long wet-dry cycles for up to 95 weeks. Damage incurred by the concrete specimens was evaluated by measuring changes to the dynamic modulus of elasticity and studying the physical appearance of the specimens after the testing period was completed.

Prismatic test specimens were used in the testing. The concrete mixture used for the specimens had a water-cement ratio of 0.45 and an air content of 6 percent. The specimens were 3 x 3 x 12 in. (7.6 x 7.6 x 30.5 cm). They were allowed to cure for 54 days before testing began.

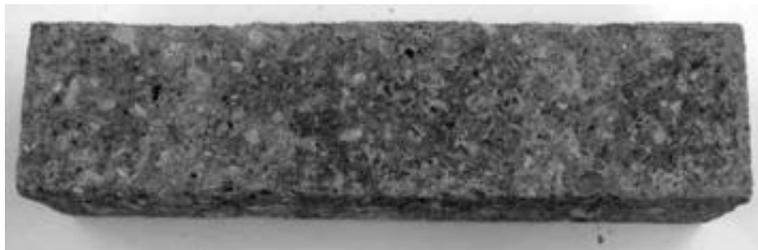
Each cycle involved submerging the specimens in the solutions for 4 days at 73°F (22.8°C) and then removing the specimens from the solutions to air dry at 100°F (37.8°C) for 3 days. After every five cycles, the deicer solutions were replaced. The dynamic modulus of elasticity of each specimen was measured before the beginning of testing and every 5 weeks at the end of the 3-day drying period. After each measurement of the dynamic modulus of elasticity, the researchers calculated the ratio ( $P_{w/d}$ ) of the dynamic modulus at the given number of cycles to the initial dynamic modulus. Testing was continued for 95 weeks or until  $P_{w/d}$  decreased below 0.9.

The researchers found that the specimens exposed to the high-concentration solutions of calcium chloride and magnesium chloride rapidly deteriorated. The dynamic modulus for these specimens decreased below 0.9 within 10 weeks of testing. The high-concentration CMA solution also deteriorated the concrete specimens. The  $P_{w/d}$  of these specimens decreased to 0.9 by the 55<sup>th</sup> week of testing. Each of the specimens subjected to calcium chloride, magnesium chloride, or CMA suffered significant scaling. Only the specimens exposed to sodium chloride endured the full 95 weeks of testing without experiencing a decrease of  $P_{w/d}$  below 0.9.

However, they did suffer some minor scaling. The specimens following testing are shown along with a specimen placed in distilled water for 95 weeks in Figures 3-3 to 3-7.



**Figure 3-3 Specimen following 95 weeks of exposure to distilled water (56).**



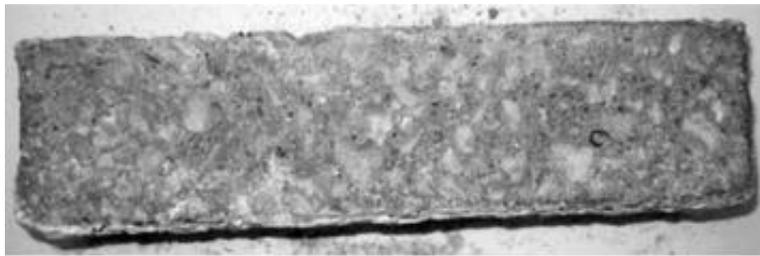
**Figure 3-4 Specimen following 95 weeks of exposure to 6.04 molal ion concentration of NaCl (56).**



**Figure 3-5 Specimen following 10 weeks of exposure to 6.04 molal ion concentration of CaCl<sub>2</sub> (56).**



**Figure 3-6 Specimen following 10 weeks of exposure to 6.04 molal ion concentration solution of  $\text{MgCl}_2$  (56).**

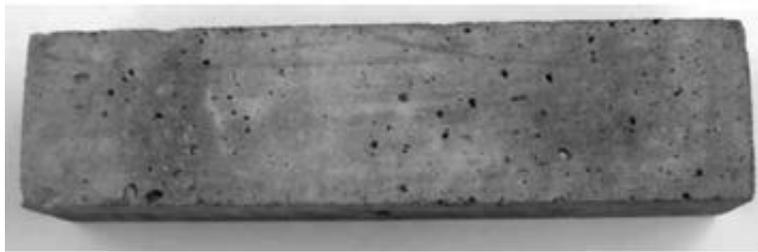


**Figure 3-7 Specimen following 60 weeks of exposure to 6.04 molal ion concentration of CMA (56).**

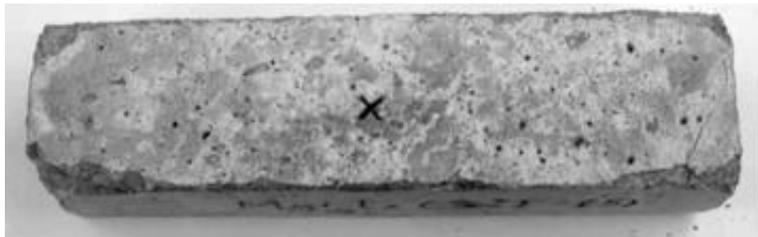
The specimens exposed to the low-concentration solutions deteriorated more slowly. The magnesium chloride and CMA-exposed specimens decreased to a  $P_{w/d}$  of 0.9 after 80 and 95 weeks of exposure, respectively. The specimens exposed to calcium chloride and sodium chloride endured the full 95 weeks. The specimens following testing are shown in Figures 3-8 to 3-11. The researchers did not identify the deterioration mechanisms that led to the deterioration of the concrete specimens in the various solutions.



**Figure 3-8 Specimen following 95 weeks of exposure to 1.06 molal ion concentration solution of NaCl (56).**



**Figure 3-9 Specimen following 95 weeks of exposure to 1.06 molal ion concentration solution of CaCl<sub>2</sub> (56).**



**Figure 3-10 Specimen following 80 weeks of exposure to 1.06 molal ion concentration solution of MgCl<sub>2</sub> (56).**



**Figure 3-11 Specimen following 95 weeks of exposure to 1.06 molal ion concentration solution of CMA (56).**

### 3.2.7 Poursaee, Laurent, and Hansson 2010

Poursaee, Laurent, and Hansson completed a study in which they investigated the effects of sodium chloride, magnesium chloride, and calcium chloride on reinforced concrete (54). They studied the effects of each of the deicers on the corrosion of steel reinforcing bars within concrete specimens. They also measured the impact of the deicers on the concrete.

The researchers prepared 6 x 6 x 4 in. (15.2 x 15.2 x 10.2 cm) mortar specimens containing four lengths of #5 rebar. One bar was placed at the top of each specimen with an upper cover depth of 0.375 in. (0.95 cm), and three bars were placed at the bottom of each specimen with a lower cover depth of 0.375 in. (0.95 cm). The bottom three bars were connected to the top bar via a 100  $\Omega$  resistor. The mortar had a water-cement ratio of 0.50.

The surface of each specimen was ponded with a salt solution equivalent to a 3 percent chloride ion concentration for 2-week periods followed by 2 weeks of drying. This exposure cycle was continued for up to 124 weeks with each specimen. After 124 weeks, the solution concentration was increased to 30 percent in order to simulate the practice of applying the deicer solutions as concentrated brines. This concentrated exposure lasted just 6 weeks, at which point the prisms exposed to calcium chloride were excessively deteriorated.

The macro-cell and micro-cell corrosion rate of the steel in each of the specimens was measured after the first week of each 2-week ponding period. For the first 60 weeks of testing,

micro-cell corrosion rates were similar for all of the specimens. After 60 weeks, the micro-cell corrosion rates increased by a factor of two to three in the specimens exposed to sodium chloride and calcium chloride. The specimens exposed to magnesium chloride remained roughly constant during this time. The researchers attributed the lack of corrosion in magnesium chloride-exposed specimens to the formation of brucite within the concrete pores, which may have limited the ingress of additional chloride ions. Only those specimens exposed to calcium chloride were observed to experience active macro-cell corrosion within the first 70 weeks of testing. When the concentration of the deicer solution was increased at 124 weeks, the corrosion rates of the steel in the specimens in calcium chloride and magnesium chloride increased rapidly; however, the corrosion rates of the specimens in sodium chloride remained constant.

Following 130 weeks of deicer exposure, the researchers observed that significant damage had occurred to the mortar specimens that had been exposed to calcium chloride and magnesium chloride. The specimens exposed to calcium chloride suffered extreme deterioration, with large cracks having developed throughout the specimens. The specimens exposed to magnesium chloride also developed cracks, although to a lesser extent. Additionally, the surfaces of the specimens exposed to magnesium chloride were observed to be severely softened upon visual inspection. No significant damage to the specimens exposed to the sodium chloride was observed, however, even after the 6 weeks of exposure at the higher concentration.

In order to identify the causes of deterioration of the specimens exposed to calcium chloride and magnesium chloride, the researchers performed X-ray diffraction analysis on cement powder samples from the specimens. They attributed the damage incurred by the specimens to the conversion of C-S-H to M-S-H caused by exposure to magnesium chloride. The formation of calcium oxychlorides within the concrete pores may also have contributed to the damage. The researchers identified the formation of calcium oxychlorides and the leaching of CH as the causes of damage in the specimens exposed to calcium chloride.

### 3.2.8 Shi et al. 2010

Shi et al. tested the physical and chemical effects of several deicers via freeze-thaw cycling (57). They cycled concrete specimens through freezing and thawing temperatures in the presence of solutions of various deicing chemicals, including sodium chloride, potassium formate, a sodium chloride-based commercial deicer, and potassium acetate-based commercial deicer, a sodium acetate/sodium formate blend, CMA, and magnesium chloride. The testing was performed on concrete specimens with a water-cement ratio of 0.51, a slump of nearly zero, an air content of 3 percent, and a 28-day compressive strength of 6,600 psi (45.5 MPa).

Deicer solutions for the experiment were prepared at concentrations of 3 percent by volume for liquid chemicals and 3 percent by mass for solids. The concrete specimens were exposed to the deicer solutions by placing the concrete on top of a saturated sponge inside a dish containing the deicer solution. Moisture loss over the course of the experimentation was prevented by covering the dish and specimen entirely with plastic wrap.

The specimens were frozen at 0°F (-17.8°C) for 17 hours, which was sufficient to freeze each of the deicer solutions. Following freezing, the specimens were placed in a 73°F (22.8°C) room for 7 hours and then returned to the freezing chamber. After every 10 cycles, the specimens were removed from the respective dishes, rinsed in water, and hand-scrubbed to remove any material loosened by the freeze-thaw cycling. The specimens were allowed to air dry for 24 hours and then weighed in order to measure the mass loss. Field emission scanning electron microscopy and energy dispersive X-ray spectroscopy were used to identify chemical changes in the concrete following the freeze-thaw cycling.

The researchers found that the specimens exposed to CMA and magnesium chloride experienced only minimal mass loss. The specimens that were exposed to potassium formate or the sodium acetate/sodium formate blend experienced 25 percent mass loss, while the specimens exposed to sodium chloride or potassium acetate showed as much as 50 percent mass loss. These results are contradictory to the trend observed in most all other experiments performed on

the effects of deicing chemicals on concrete, with sodium chloride unexpectedly causing the most damage and magnesium chloride causing the least.

While chemical changes did occur to the concrete, the primary damage to the specimens was caused by physical mechanisms. Because the researchers used diluted solutions and exposed the concrete to the test solutions only through a saturated sponge, significant chemical reactions within the concrete could not occur. Additionally, the production of brucite by the magnesium chloride and CMA solutions in the concrete specimens may have prevented significant penetration of the solutions into the specimens over time.

### 3.2.9 Shi et al. 2011

In a second study, Shi et al. specifically investigated the effects of continuous deicer exposure on concrete strength and chemistry (14). The researchers ponded two different types of concrete specimens under deicer solutions for 338 days at room temperature. The deicers investigated were sodium chloride, sodium chloride with a reinforcing steel corrosion inhibitor, calcium chloride with a reinforcing steel corrosion inhibitor, and magnesium chloride with a reinforcing steel corrosion inhibitor. The concrete specimens were exposed to solutions prepared at concentrations of 8 percent by mass of each deicer.

Concrete specimens used in the study were designed to simulate Washington State Department of Transportation bridge decks and roadway pavements constructed before the 1980s. The bridge deck concrete mixture had a water-cement ratio of 0.38, while the pavement concrete mixture had a water-cement ratio of 0.39. Each of the mixtures had an air content of 5 percent.

Following the 338 days of deicer ponding exposure, the concrete specimens were subjected to compression testing. The pavement mixture specimens maintained or increased their strength through the period of deicer exposure except for the specimens exposed to the magnesium chloride solution. The magnesium chloride-exposed specimens experienced a significant loss in compressive strength. For the bridge mixture, the ponding regimen led to strength loss in each of the specimens. The magnesium chloride solution was the most

deleterious, followed by the two sodium chloride solutions and the calcium chloride solution. The calcium chloride solution had a significantly smaller effect than the other solutions.

A few of the exposed specimens from each of the solutions were withheld from the compression testing. The withheld specimens were examined using field emission scanning electron microscopy and energy dispersive X-ray spectroscopy in order to determine the nature of the chemical effects of each of the deicer solutions on the concrete specimens.

The researchers found that the sodium chloride solutions had damaged the concrete primarily through decalcification. In the specimens exposed to the calcium chloride solution, the researchers found that calcium oxychloride formation and some leaching of CH from the concrete had led to the concrete damage; however, they suggested that calcium ions had also played a beneficial role in helping the concrete maintain its integrity. In the magnesium chloride-exposed specimens, conversion of C-S-H to M-S-H and formation of brucite were identified as damage mechanisms. The researchers found that the magnesium chloride led to concrete volume change, loss of compressive strength, and microcracking.

#### 3.2.10 Jain et al. 2012

Jain et al. performed several experiments to investigate the effects of sodium chloride, calcium chloride, and magnesium chloride on the physical properties of concrete (58). They used wet-dry, freeze-thaw, and soak regimens on two types of concrete. The two types of concrete were a plain concrete produced using Type I portland cement and a fly ash concrete, which had 20 percent by mass of the Type I cement replaced with Class C fly ash in the mixture.

Three different types of specimens were created for the study, including 3 x 3 x 11.5 in. (7.6 x 7.6 x 29.2 cm) prisms, 4 x 8 in. (10.2 x 20.3 cm) cylinders, and 3 x 6 in. (7.6 x 15.2 cm) cylinders. For the wet-dry regime, the sodium chloride solution had a concentration of 23 percent, the magnesium chloride solution had a concentration of 25 percent, and the calcium chloride solution had a concentration of 28 percent. For the freeze-thaw regime, the sodium chloride solution had a concentration of 14 percent, the magnesium chloride solution had a concentration of 15 percent, and the calcium chloride solution had a concentration of 17 percent,

all by mass. The concentration levels were selected based on actual deicer usage rates in the field.

The specimens subjected to wet-dry cycling were immersed in their solutions for 16 hours at 39.2°F (4°C) and dried at 73.4°F (23°C) and 50 percent relative humidity for 8 hours during each cycle. For the specimens subjected to freeze-thaw cycling, the specimens were immersed in their solutions and subjected to 9 hours of cooling from 71.6°F (22°C) to -4°F (-20°C), 5 hours of exposure at -4°F (-20°C), 6 hours of heating from -4°F (-20°C) to 71.6°F (22°C), and 4 hours of exposure at 71.6°F (22°C).

Physical changes in the specimens were observed every 2 weeks by measuring the resonant frequencies, ultrasonic pulse velocities, and changes in mass of the specimens. Following completion of the exposure regimes, the compressive strength of the specimens was measured.

The specimens were subjected to wet-dry or freeze-thaw cycling for up to 350 cycles. However, exposure to the calcium chloride was ended after only 168 cycles because those specimens were undergoing rapid deterioration.

Calcium chloride was found to be the most harmful of the solutions tested. Specimens exposed to calcium chloride exhibited 15 percent reductions in resonant frequency values after as few as 154 cycles. Similar damage was incurred by specimens exposed to the magnesium chloride solutions; however, the damage occurred at a slower rate. Three hundred cycles were required to cause a similar reduction in resonant frequency values in the specimens exposed to magnesium chloride. No significant changes were observed in the specimens exposed to sodium chloride solutions.

### **3.3 Summary**

Researchers have performed numerous studies to directly compare the effects of various deicers on concrete. Many strategies have been used to simulate the environmental conditions

experienced by concrete pavements. Most strategies involve freeze-thaw cycling, wet-dry cycling, and/or soaking mortar or concrete specimens. Freeze-thaw cycling tends to magnify the physical effects of the deicers investigated, while wet-dry cycling and soaking allow chemical effects to be investigated without the effects of frost action masking the results.

Regardless of variations in testing methods and specimen characteristics, the results from nine of the ten studies summarized in this research indicate that specimens exposed to sodium chloride experienced only minor, if any, adverse effects, while specimens exposed to calcium chloride, magnesium chloride, or CMA experienced significant deterioration, including scaling, cracking, mass loss, and compressive strength loss. The researchers found that the deterioration suffered by specimens exposed to calcium chloride was caused by the formation of calcium oxychloride and complex salts, while specimens exposed to magnesium chloride and CMA deteriorated because of M-S-H and brucite formation.

## **4.0 CONCLUSION**

### **4.1 Summary**

The purpose of this research was to conduct a thorough review of the literature and summarize the effects of several commonly used deicers on concrete pavement. Sodium chloride, calcium chloride, magnesium chloride, and CMA and the effects of their respective ions were specifically discussed. All of the studies known to the authors that have been performed to compare the effects of various deicers were summarized, including 10 different comparative studies published between 1995 and 2012.

### **4.2 Findings**

Deicers can affect concrete both physically and chemically. Physical effects are typically manifested as cracking and salt scaling. Several mechanisms have been proposed to explain the phenomenon of salt scaling, including thermal shock, precipitation and growth of salt crystals, osmotic pressure, and glue spalling.

The chemical effects of deicers are often overshadowed by the physical effects, but they can be significant nonetheless. Reactions may involve cement hydration products, aggregates, or reinforcing steel. Reactions caused by deicer ions include the leaching of CH from the paste, the decalcification of C-S-H, the conversion of C-S-H to M-S-H, and the formation of brucite, complex salts, and oxychlorides. ASR and ACR can be initiated and accelerated by alkalis from deicers. Accumulation of critical concentrations of chloride ions in the vicinity of the steel can initiate corrosion.

Researchers have performed numerous studies to directly compare the effects of various deicers on concrete. Many strategies have been used to simulate the environmental conditions experienced by concrete pavements. Most strategies involve freeze-thaw cycling, wet-dry cycling, and/or soaking mortar or concrete specimens. Freeze-thaw cycling tends to magnify the

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### **4.3 Recommendations**

Given the results of this literature review, engineers responsible for winter maintenance of concrete pavements should utilize sodium chloride whenever possible, instead of calcium chloride, magnesium chloride, or CMA, and apply only the amount that is absolutely necessary to ensure the safety of the traveling public. In addition, when new winter maintenance treatments are considered, the chemical composition of the treatments should be carefully evaluated with respect to the potential damage that may be caused to the pavement.

To quantify the adverse effects of deicer applications on concrete pavement service life, further research is recommended. Understanding the degree of deterioration caused by deicer treatments would help pavement managers more accurately anticipate maintenance, rehabilitation and replacement actions and more accurately calculate life-cycle costs for concrete pavements.

## REFERENCES

1. Salt Institute. *Winter Road Safety*. <http://www.saltinstitute.org/Uses-benefits/Winter-road-safety>. Accessed February 1, 2012.
2. Hassan, Y., A. O. A. El Halim, A. G. Razaqpur, W. Bekheet, and M. H. Farha. Effects of Runway Deicers on Pavement Materials and Mixes: Comparison with Road Salt. *Journal of Transportation Engineering*, Vol. 128, No. 4, 2002, pp. 385-391.
3. Mindess, S., J. F. Young, and D. Darwin. *Concrete*. Prentice Hall, 2003.
4. Pigeon, M., and R. Pleau. *Durability of Concrete in Cold Climates*. E & FN SPON, London, United Kingdom, 1995.
5. Harnick, A. B., V. Meier, and A. Rosli. Combined Influence of Freezing and Deicing Salt on Concrete: Physical Aspects. *Durability of Building Materials and Components*. London, United Kingdom, 1980.
6. Hansen, W. C. Crystal Growth as a Source of Expansion in Portland-Cement Concrete. In *Proceedings of American Society for Testing and Materials*. Philadelphia, PA, 1963.
7. Chatterji, S., and N. Thaulow. Unambiguous Demonstration of Destructive Crystal Growth Pressure. *Cement and Concrete Research*, Vol. 27, No. 6, 1997, pp. 811-816.
8. Scherer, G. W. Stress from Crystallization of Salt. *Cement and Concrete Research*, Vol. 34, No. 9, 2004, pp. 1613-1624.
9. Yang, Q., X. Wu, and S. Huang. Concrete Deterioration Due to Physical Attack by Salt Crystallization. In *10th International Congress on the Chemistry of Cement*. Gothenburg, Sweden, 1997.
10. Flatt, R. J. Salt Damage in Porous Materials: How High Supersaturations Are Generated. *Journal of Crystal Growth*, Vol. 242, No. 2002, pp. 435-454.

11. Powers, T. C. Freezing Effects in Concrete. *Durability of Concrete*. American Concrete Institute, Detroit, MI, 1975.
12. Valenza II, J. J., and G. W. Scherer. A Review of Salt Scaling: Ii. Mechanisms. *Cement and Concrete Research*, Vol. 37, No. 7, 2007, pp. 1022-1034.
13. Marchand, J., M. Pigeon, D. Bager, and C. Talbot. Influence of Chloride Solution Concentration on Deicer Salt Scaling Deterioration of Concrete. *ACI Materials Journal*, Vol. 96, No. 4, 1999, pp. 7.
14. Shi, X., L. Fay, M. M. Peterson, M. Berry, and M. Mooney. A FESEM/EDX Investigation into How Continuous Deicer Exposure Affects the Chemistry of Portland Cement Concrete. *Construction and Building Materials*, Vol. 25, No. 2, 2011, pp. 957-966.
15. Chatterji, S. Mechanism of the  $\text{CaCl}_2$  Attack on Portland Cement Concrete. *Cement and Concrete Research*, Vol. 8, No. 4, 1978, pp. 461-467.
16. Frigione, G., and R. Sersale. The Action of Some Aggressive Solutions on Portland, Pozzolanic and Blastfurnace Slag Cement Mortars. *Cement and Concrete Research*, Vol. 19, No. 6, 1989, pp. 885-893.
17. Ftikos, C., and G. Parissakis. The Combined Action of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  Ions in Cement Pastes. *Cement and Concrete Research*, Vol. 15, No. 4, 1985, pp. 593-599.
18. Moukwa, M. Characteristics of the Attack of Cement Paste by  $\text{MgSO}_4$  and  $\text{MgCl}_2$  from the Pore Structure Measurements. *Cement and Concrete Research*, Vol. 20, No. 1, 1990, pp. 148-158.
19. Wang, K., D. E. Nelsen, and W. A. Nixon. Damaging Effects of Deicing Chemicals on Concrete Materials. *Cement and Concrete Composites*, Vol. 28, No. 2, 2006, pp. 173-188.

20. Carde, C., R. François, and J.-M. Torrenti. Leaching of Both Calcium Hydroxide and C-S-H from Cement Paste: Modeling the Mechanical Behavior. *Cement and Concrete Research*, Vol. 26, No. 8, 1996, pp. 1257-1268.
21. Carde, C., and R. François. Modeling the Loss of Strength and Porosity Increase Due to the Leaching of Cement Pastes. *Cement & Concrete Composites*, Vol. 21, No. 1999, pp. 8.
22. Carde, C., and R. François. Effect of the Leaching of Calcium Hydroxide from Cement Paste on Mechanical and Physical Properties. *Cement and Concrete Research*, Vol. 27, No. 4, 1997, pp. 539-550.
23. Kendall, K., A. J. Howard, J. D. Birchall, P. L. Pratt, B. A. Proctor, and S. A. Jefferis. The Relation between Porosity, Microstructure and Strength, and the Approach to Advanced Cement-Based Materials [and Discussion]. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 310, No. 1511, 1983, pp. 139-153.
24. Santagata, M. C., and M. Collepardi. The Effect of CMA Deicers on Concrete Properties. *Cement and Concrete Research*, Vol. 30, No. 9, 2000, pp. 1389-1394.
25. Heukamp, F. H., F. J. Ulm, and J. T. Germaine. Mechanical Properties of Calcium-Leached Cement Pastes: Triaxial Stress States and the Influence of the Pore Pressures. *Cement and Concrete Research*, Vol. 31, No. 5, 2001, pp. 767-774.
26. Kurdowski, W. The Protective Layer and Decalcification of C-S-H in the Mechanism of Chloride Corrosion of Cement Paste. *Cement and Concrete Research*, Vol. 34, No. 9, 2004, pp. 1555-1559.
27. Mussato, B., O. Gepraegs, and G. Farnden. Relative Effects of Sodium Chloride and Magnesium Chloride on Reinforced Concrete: State of the Art. *Transportation Research Record*, Vol. No. 1866, 2004, pp. 8.

28. Brown, P. W., and A. Doerr. Chemical Changes in Concrete Due to the Ingress of Aggressive Species. *Cement and Concrete Research*, Vol. 30, No. 3, 2000, pp. 411-418.
29. Kozikowski, R. L., P. C. Taylor, and W. A. Pyć. *Evaluation of Potential Concrete Deterioration Related to Magnesium Chloride (MgCl<sub>2</sub>) Deicing Salts*. Portland Cement Association, Skokie, IL, 2007.
30. Cody, R. D., A. M. Cody, P. G. Spry, and G.-L. Gan. Experimental Deterioration of Highway Concrete by Chloride Deicing Salts. *Environmental & Engineering Geoscience*, Vol. 2, No. 1996, pp. 14.
31. Lee, H., A. M. Cody, R. D. Cody, and P. G. Spry. PCC Pavement Deterioration and Expansive Mineral Growth. In *Crossroads 2000*. Iowa State University, Ames, IA, 1998.
32. Lee, H., R. D. Cody, A. M. Cody, and P. G. Spry. Effects of Various Deicing Chemicals on Pavement Concrete Deterioration. In *Mid-Continent Transportation Symposium*. Iowa State University, Ames, IA, 2000.
33. Cody, R. D., P. G. Spry, A. M. Cody, and G.-L. Gan. *The Role of Magnesium in Concrete Deterioration*. I. D. o. Transportation, 1994.
34. Sutter, L., T. Van Dam, K. Peterson, and D. Johnston. Long-Term Effects of Magnesium Chloride and Other Concentrated Salt Solutions on Pavement and Structural Portland Cement Concrete: Phase I Results. *Transportation Research Record*, Vol. 1979, No. 2006, pp. 60-68.
35. Browne, F. P., and P. D. Cady. *Deicer Scaling Mechanisms in Concrete*. American Concrete Institute, Detroit, MI, 1975.
36. Berntsson, L., and S. Chandra. Damage of Concrete Sleepers by Calcium Chloride. *Cement and Concrete Research*, Vol. 12, No. 1, 1982, pp. 87-92.

37. Monosi, S., and M. Collepardi. Research on  $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$  Identified in Concrete Damaged by  $\text{CaCl}_2$  Attack. *Il Cemento*, Vol. 87, No. 1990, pp. 3-8.
38. Sutter, L., K. Peterson, S. Touton, T. Van Dam, and D. Johnston. Petrographic Evidence of Calcium Oxychloride Formation in Mortars Exposed to Magnesium Chloride Solution. *Cement and Concrete Research*, Vol. 36, No. 8, 2006, pp. 1533-1541.
39. Chatterji, S., A. D. Jensen, N. Thaulow, and P. Christensen. Studies of Alkali-Silica Reaction. Part 3. Mechanisms by Which  $\text{NaCl}$  and  $\text{Ca}(\text{OH})_2$  Affect the Reaction. *Cement and Concrete Research*, Vol. 16, No. 1986, pp. 9.
40. Bérubé, M. A., J. F. Dorion, J. Duchesne, B. Fournier, and D. Vézina. Laboratory and Field Investigations of the Influence of Sodium Chloride on Alkali-Silica Reactivity. *Cement and Concrete Research*, Vol. 33, No. 1, 2003, pp. 77-84.
41. Chatterji, S., N. Thaulow, and A. D. Jensen. Studies of Alkali-Silica Reaction. Part 4. Effect of Different Alkali Salt Solutions on Expansion. *Cement and Concrete Research*, Vol. 17, No. 1987, pp. 7.
42. Duchesne, J., and M. A. Bérubé. Effect of the Cement Chemistry and the Sample Size on ASR Expansion of Concrete Exposed to Salt. *Cement and Concrete Research*, Vol. 33, No. 5, 2003, pp. 629-634.
43. Katayama, T., M. Tagami, Y. Sarai, S. Izumi, and T. Hira. Alkali-Aggregate Reaction under the Influence of Deicing Salts in the Hokuriku District, Japan. *Materials Characterization*, Vol. 53, No. 2-4, 2004, pp. 105-122.
44. Kawamura, M., and S. Komatsu. Behavior of Various Ions in Pore Solution in  $\text{NaCl}$ -Bearing Mortar with and without Reactive Aggregate at Early Ages. *Cement and Concrete Research*, Vol. 27, No. 1, 1997, pp. 29-36.
45. Nixon, P. J., C. Page, I. Canham, and R. Bollinghaus. Influence of Sodium Chloride on the ASR. *Advances in Cement Research*, Vol. 1, No. 1988, pp. 99-105.

46. Rangaraju, P. R., K. R. Sompura, and J. Olek. Investigation into Potential of Alkali-Acetate-Based Deicers to Cause Alkali-Silica Reaction in Concrete. *Transportation Research Record*, Vol. 1979, No. 2006, pp. 69-78.
47. Kawamura, M., and M. Ichise. Characteristics of Alkali-Silica Reaction in the Presence of Sodium and Calcium Chloride. *Cement and Concrete Research*, Vol. 20, No. 5, 1990, pp. 757-766.
48. Kawamura, M., K. Takeuchi, and A. Sugiyama. Mechanisms of Expansion of Mortars Containing Reactive Aggregate in NaCl Solution. *Cement and Concrete Research*, Vol. 24, No. 4, 1994, pp. 621-632.
49. Dubberke, W., and V. J. Marks. The Effect of Deicing Salt on Aggregate Durability. *Transportation Research Record*, Vol. No. 1031, 1985, pp. 27-34.
50. Young, J. F., S. Mindess, R. J. Gray, and A. Bentur. *The Science and Technology of Civil Engineering Materials*. Prentice-Hall, Inc., Upper Saddle River, NJ, 1998.
51. Richardson, M. G. *Fundamentals of Durable Reinforced Concrete*. Spon Press, New York, NY, 2002.
52. Hansson, C. M., T. Frolund, and J. B. Markussen. The Effect of Chloride Cation Type on the Corrosion of Steel in Concrete by Chloride Salts. *Cement & Concrete Composites*, Vol. 15, No. 1, 1985, pp. 65-73.
53. Pruckner, F., and O. E. Gjrv. Effect of CaCl<sub>2</sub> and NaCl Additions on Concrete Corrosivity. *Cement and Concrete Research*, Vol. 34, No. 7, 2004, pp. 1209-1217.
54. Poursaee, A., A. Laurent, and C. M. Hansson. Corrosion of Steel Bars in OPC Mortar Exposed to NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>: Macro- and Micro-Cell Corrosion Perspective. *Cement and Concrete Research*, Vol. 40, No. 3, 2010, pp. 426-430.

55. Peterson, O. Chemical Effects on Cement Mortar of Calcium Magnesium Acetate as a Deicing Salt. *Cement and Concrete Research*, Vol. 25, No. 3, 1995, pp. 617-626.
56. Darwin, D., J. Browning, L. Gong, and S. R. Hughes. Effects of Deicers on Concrete Deterioration. *ACI Materials Journal*, Vol. 105, No. 6, 2008, pp. 622-627.
57. Shi, X., L. Fay, M. M. Peterson, and Z. Yang. Freeze-Thaw Damage and Chemical Change of a Portland Cement Concrete in the Presence of Diluted Deicers. *Materials and Structures*, Vol. 43, No. 7, 2010, pp. 933-946.
58. Jain, J., J. Olek, A. Janusz, and D. Jozwiak-Niedzwiedzka. Effects of Deicing Salt Solutions on Physical Properties of Pavement Concretes. *Transportation Research Record*, Vol. 2290, No. 2012, pp. 69-75.