

CHEMICAL DEICERS AND CONCRETE PAVEMENT: IMPACTS AND MITIGATION

INTRODUCTION

This Tech Brief focuses on a recently recognized form of deterioration on concrete pavements referred to as chemical deicer distress. It is gaining attention due to the increased frequency and severity of its appearance, which is related to the increased use of aqueous solutions of calcium chloride (CaCl_2) and magnesium chloride (MgCl_2) for pavement deicing (Sutter et al. 2008; Weiss and Farnam 2015). The resulting pavement distress often first appears as a “shadowing” at the pavement joints, which progresses into disintegration of the concrete as shown in figure 1 (Taylor, Sutter, and Weiss 2012). This Tech Brief summarizes the use of chemical anti-icers and deicers, reviews how hydraulic cement paste (HCP) is traditionally protected from freeze-thaw damage, describes physical and chemical distress mechanisms in the presence of aqueous CaCl_2 or MgCl_2 brine solutions, and discusses strategies that can be employed to mitigate this distress.



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Figure 1. Joint “shadowing” (left) and eventual disintegration of concrete at joint (right).

ANTI-ICING AND DEICING PRACTICES

A primary responsibility of any State Highway Agency (SHA) is keeping roads safe for the traveling public. This responsibility becomes especially acute during inclement winter weather when the accumulation of snow and ice on the surfaces of roads and bridges can result in a dramatic loss of surface friction, creating hazardous driving conditions. SHAs use a variety of means to maintain a safe riding surface, including plowing, the application of abrasives (e.g., sand), and the use of chemicals that depress the freezing temperature of water, thus melting snow and ice. If these chemicals are applied prior to a winter precipitation event, the activity is referred to as *anti-icing* because it is designed to prevent ice accumulation or assist in ice removal by reducing the bond between the ice and the pavement surface. If applied to remove snow and ice after accumulation begins, the activity is referred to as *deicing*.

Anti-icing and deicing are largely accomplished through the application of one or more chemicals. These may be solids or liquids, and may be combined with abrasives to help establish traction. Commonly used liquids are aqueous solutions of chlorides (e.g., sodium chloride [NaCl], MgCl_2 , and CaCl_2) or other chemicals such as calcium magnesium acetate (CMA), potassium acetate (KAc), and urea. The effectiveness of these chemicals to melt ice over a range of temperatures is directly related to the type of chemical and its concentration, information that is readily available to winter maintenance personnel.



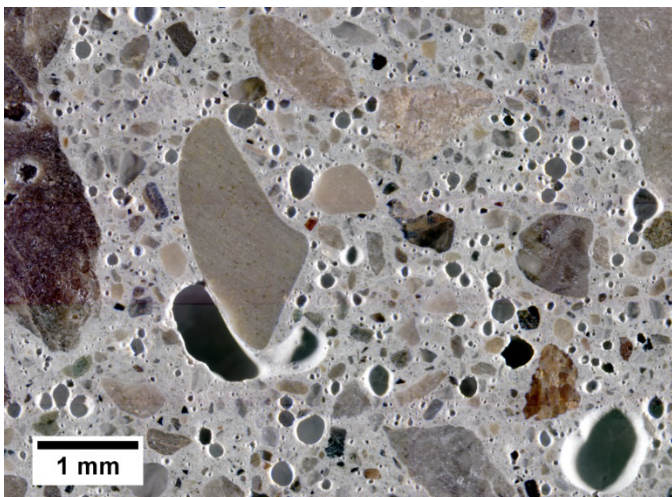
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In the last decade, concerns have been raised regarding the potential for deleterious effects of certain chemical deicers (most notably $MgCl_2$ and $CaCl_2$) on concrete. Chemical deicers based on $MgCl_2$ and $CaCl_2$ are becoming increasingly popular due to their relatively low cost, ease of use, and effectiveness over a broad range of temperatures (Sutter et al. 2008; Taylor, Sutter, and Weiss 2012; Weiss and Farnam 2015). As aqueous solutions, they are commonly applied at relatively high concentrations to dry pavement as anti-icing agents prior to a winter precipitation event, a practice that can result in direct absorption of the solutions at full concentration into the pavement surface and joints. $MgCl_2$ and $CaCl_2$ can also be used as prewetting agent mixed with dry NaCl crystals to help them stick to the pavement surface and in a dry mix with NaCl (typically 20 percent $MgCl_2$ or $CaCl_2$ and 80 percent NaCl) to increase the effectiveness of the deicer.

HYDRATED CEMENT PASTE AND FREEZE-THAW DAMAGE

Traditionally, the durability of HCP under a freeze-thaw environment has been closely linked to the size and volume of the entrained air bubbles in the concrete (ACI 2016; Kosmatka and Wilson 2016). These air bubbles are purposely formed in the fresh concrete during mixing through the addition of an air-entraining admixture (AEA) conforming to AASHTO M 154 or ASTM C260/C260 M. Most entrained air bubbles range in size from 10 to 100 μm (Kosmatka and Wilson 2016) and, ideally, are uniformly dispersed throughout the HCP, as shown in figure 2. The air void system required to protect concrete from freeze-thaw damage is commonly linked to exposure conditions, the most severe of which is when deicers are present (ACI 2016; Kosmatka and Wilson 2016). Specific requirements regarding the characteristics of the air-void system needed to protect the HCP from freeze-thaw damage are provided in a separate FHWA Tech Brief (Van Dam 2016), but typically include air contents ranging from 5 to 8 percent.



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Figure 2. Stereo micrograph of entrained air-void system (spherical bubbles) in hardened concrete. Larger, irregular voids are entrapped air.

In addition to the entrained air-void system, a maximum water-to-cementitious materials ratio (w/cm) is also typically specified. This is a recognition that the overall porosity of the HCP decreases as w/cm decreases, resulting in a decrease in permeability and an increase in strength. ACI (2016) recommends a maximum w/cm of 0.45 (for plain concrete) if freeze-thaw conditions are to be encountered. Furthermore, if the pavement is to be hand finished, the supplementary cementitious materials (SCM) content is limited to a maximum of 25 percent fly ash or 50 percent slag cement by mass of total cementitious materials. ACI (2016) recognizes that formed and machine-finished surfaces, such as slip-formed pavement surfaces, are not greatly at risk of scaling and these SCM limits are not applied.

In summary, traditional freeze-thaw damage in the HCP is mitigated primarily through the creation of an effective entrained air-void system in the concrete, in which the spherical air voids are spaced closely enough to relieve the stress generated as the pore solution freezes. Current guidance suggests that the total volume of entrained air should be increased and the maximum allowable w/cm should be reduced as environmental conditions become more severe (i.e., with increasing availability of water and, especially, the presence of chemical deicers). Historically, this strategy has been largely effective as long as the desired air-void system parameters were achieved and traditional deicing practices were used.

DEICER DISTRESS MECHANISMS

Physical Mechanisms

It has long been recognized that chemical deicer applications amplify the physical mechanisms responsible for freeze-thaw deterioration of concrete (ACI 2016). This amplification is thought to be due to multiple factors, including the increased level of saturation that occurs when salt solutions are present, thermal shock that occurs due to the phase change of ice to water, an increase in osmotic pressures due to changes in pore solution chemistry, and the potential for salt crystallization within confined pore spaces (Mindess, Young, and Darwin 2003; ACI 2016; Kosmatka and Wilson 2016). As such, the exposure to chemical deicers constitutes the most severe freeze-thaw exposure condition based on ACI (2016). To address this, current recommendations are that the concrete must be air entrained (with a total air content of 6 ± 1.5 percent for typical paving and bridge deck concrete, with some agencies assessing air content after placement) and must have a w/cm below 0.45 (for plain concrete, whereas a value of 0.40 is recommended for reinforced concrete) to prevent damage from the application of deicers (ACI 2016). Until recently, the most common distress associated with deicer applications on concrete flatwork, such as slabs, has been surface scaling, such as shown in figure 3. The strategies described above have historically been effective in minimizing the occurrence of deicer scaling on machine-finished SHA pavements and bridge decks when accompanied with good finishing and curing practices.



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Figure 3. Concrete surface suffering deicer scaling.

However, there has been a recent increase in deterioration observed in the vicinity of concrete joints. As illustrated in figure 1 (presented earlier), this distress differs from scaling in that it initiates and progresses at joint locations. It often first appears as a “darkening” or “shadowing” of the concrete adjacent to the joint, which is attributed to water being trapped in microcracks that have developed near the joints. Over time, this microcracking may progress into significant loss of material (Taylor, Sutter, and Weiss 2012; Weiss and Farnam 2015). Physical mechanisms of this joint deterioration have been linked to the following factors, often working in combination (Taylor, Sutter, and Weiss 2012):

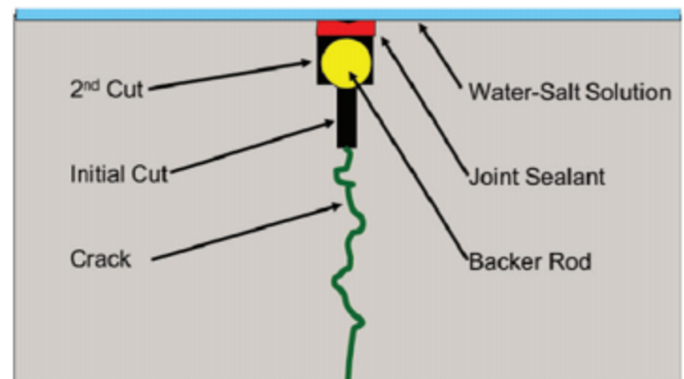
- Locally saturated concrete in the vicinity of the joint.
- Presence of a marginal-to-inadequate entrained air-void system.
- A w/cm greater than 0.40.
- Aggressive use of chemical deicers.
- The presence of coarse aggregates that are slowly susceptible to freeze-thaw damage (i.e., D-cracking).

The deterioration in the study by Taylor, Sutter, and Weiss (2012) was commonly observed in the joint below the pavement surface, being related to a combination of factors including the ponding of water in the bottom of the saw cut, salts collecting in the joints, and increased permeability at the cut faces of the joints. The role of deicers in the occurrence of this deterioration was noted in the report, which states (Taylor, Sutter, and Weiss 2012):

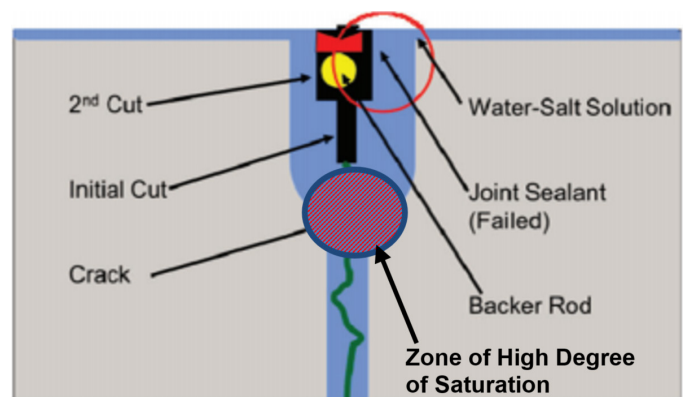
The effects of deicing salts are likely the tipping point, explaining why this is perceived as a relatively new phenomenon. It is likely that this form of distress has been occurring for a long time, but the change in salting practices have made it more common and, therefore, more notable than before.

It is recognized that partially dry concrete will not be damaged from freeze-thaw cycles because the larger pores in the HCP are empty and provide adequate space to accommodate hydraulic and osmotic pressures that develop as ice forms. But if this same concrete undergoes freezing and thawing in a critically saturated state (above approximately 86 percent saturation), damage will occur within even a single freeze-thaw cycle, irrespective of air void volume (Jones et al. 2013).

Critical saturation of concrete is more likely to occur at joint locations for a number of reasons, schematically illustrated in figure 4, which shows a typical sawed and sealed contraction joint in concrete. A properly functioning sealed joint (figure 4a) will significantly reduce the ingress of the water-salt deicer solution so that very little additional saturation of the concrete occurs within the joint. If the joint seal is compromised (figure 4b), the deicer solution will penetrate into the joint, increasing the saturation of the surrounding concrete as illustrated. If the material beneath the activated joint is not free-draining, water entering through the compromised sealant will not be able to drain from the joint. This can lead to critical saturation of the concrete. In this case, a sufficiently low w/cm and an adequate entrained air-void system are essential to protect the concrete against freeze-thaw damage.



(a)



(b)

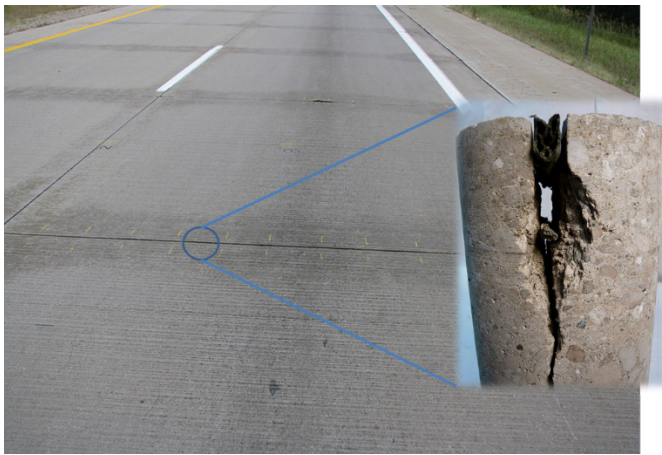
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Figure 4. A good performing sawed contraction joint in concrete (a) does not allow water to enter the joint. Once the joint seal fails (b), the water-salt solution can enter the joint and saturate the adjacent concrete if not drained (Jones et al. 2013).

Yet there are a number of conditions that may occur that, in combination, may result in the deicer solution remaining in the joint for long periods of time, including (Taylor, Sutter, and Weiss 2012; Jones et al. 2013):

- The joint does not activate and a crack does not form.
- The joint is highly restrained, due to poor tie bar design or misaligned dowels, and thus does not open sufficiently to drain.
- The crack of an activated joint becomes clogged and will not drain.
- The presence of the failed sealant and backer rod delay the evaporation of the solution that is retained within the joint.

Once the water-salt solution pools within the joint, it is absorbed into the exposed concrete and becomes increasingly concentrated over time as additional deicing salts are used (Jones et al. 2013; Weiss and Farnam 2015; Monical et al. 2016). If the joint is not draining, the greatest degree of saturation occurs in a zone at the bottom of the first saw cut, as shown in figure 4b. Due in part to the properties of salt solutions, which increase the degree of saturation, this may result in the concrete within this zone exceeding critical saturation (Jones et al. 2013; Monical et al. 2016). Figure 5 illustrates the type of damage that can occur in this zone of critically high saturation.



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Figure 5. Joints on I-94 in Michigan showing surface "shadowing." Extracted core reveals high degree of damage below the surface in zone of high degree of saturation (courtesy Dr. Karl Peterson).

Chemical Mechanisms

In addition to the amplification of physical freeze-thaw damage, the potential for chemical attack associated with deicing salts was also noted by Taylor, Sutter, and Weiss (2012) and by Jones et al. (2013). Chemical deicer attack is a relatively new area of concern, at least partially spurred on by the increasing use of aqueous solutions of CaCl_2 and MgCl_2 as pavement deicers (Sutter et al. 2006; Jones et al. 2013; Weiss and Farnam 2015). An understanding of the mechanisms responsible for this

form of attack is currently emerging and the true extent of risk to concrete pavement performance is being studied. Nevertheless, many consider it prudent to consider the potential for this type of chemical deicer attack when designing concrete pavements that will be subjected to these types of deicing chemicals.

It is known that reactions can occur between various deicers and a number of phases in HCP, including reactions with the tri-calcium aluminate phase to form Friedel's salt or Kuzel's salt. Yet the primary mechanism thought to be responsible for chemical deicer attack is a phase change that occurs in the presence of water, in which the calcium hydroxide present in typical HCP reacts with CaCl_2 to form calcium oxychloride (Sutter et al. 2006; Sutter et al. 2008; Weiss and Farnam 2015; Monical et al. 2016). The source of CaCl_2 can be directly from CaCl_2 -based deicers or as a product of chemical reactions that occur between MgCl_2 found in MgCl_2 -based deicers and calcium hydroxide and calcium-silicate hydrate present in HCP (Sutter et al. 2008). The phase change to calcium oxychloride is highly expansive, with the resulting damage to the HCP likely due to crystallization pressures. Figure 6 shows the effect of this expansive reaction on cylinders of mortar soaked in solutions of CaCl_2 and MgCl_2 at 40 °F (4 °C) (Sutter et al. 2008). Scanning electron microscopy (see figure 7) shows that the distress occurred in specimens soaked in CaCl_2 and MgCl_2 solutions and is characterized by radial cracking from the outside of the cylinders inward, as if the surface were peeling away like layers of an onion. Further, affected areas of the HCP are altered, becoming more porous and nearly devoid of calcium hydroxide (Sutter et al. 2008).

Depending on the salt concentration in the solution, the phase change to calcium oxychloride occurs above the freezing point of pure water at temperatures between 32 °F and 122 °F (0 °C and 50 °C) (Weiss and Farnam 2015). At low salt concentrations, the chemical reaction may not occur at all and any distress that occurs will largely be due to physical freeze-thaw deterioration. As salt concentration increases, the chemical attack mechanism may become a more important, if not dominant, factor.

The importance of salt concentration in the solutions of CaCl_2 and MgCl_2 cannot be overstated. Deicers are applied at concentrations well in excess of what is needed for the calcium oxychloride phase change to occur. When these solutions are used in anti-icing operations, they remain at full concentration until becoming diluted as the precipitation event occurs, if it occurs at all. Further, anti-icing is often done when the pavement is dry prior to the start of the event, and thus the fully concentrated salt solutions can be drawn into the dry concrete through sorption. Sorption would be especially high if the solutions pool in non-draining joints. When used as deicers applied during or after a precipitation event, the melting of ice dilutes the solution and decreases the potential for an occurrence of a deleterious chemical reaction. But, as described previously, salts may concentrate over time if the solution is retained in the joint and the deicing cycle repeated, resulting in the potential for a damaging chemical reaction.

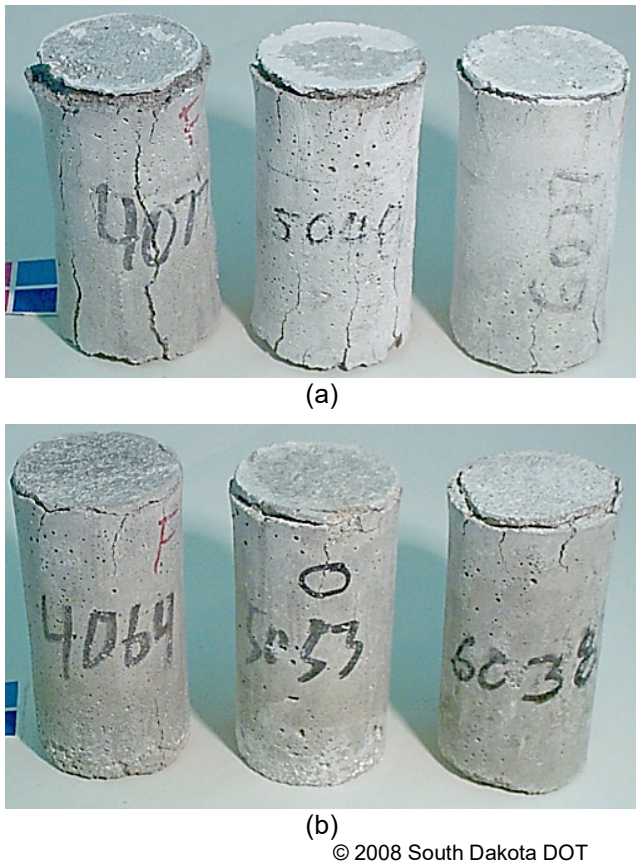


Figure 6. Expansion in mortar specimens soaked in (a) CaCl_2 and (b) MgCl_2 for 84 days at 40 °F. Note that these specimens were never frozen (Sutter et al. 2008).

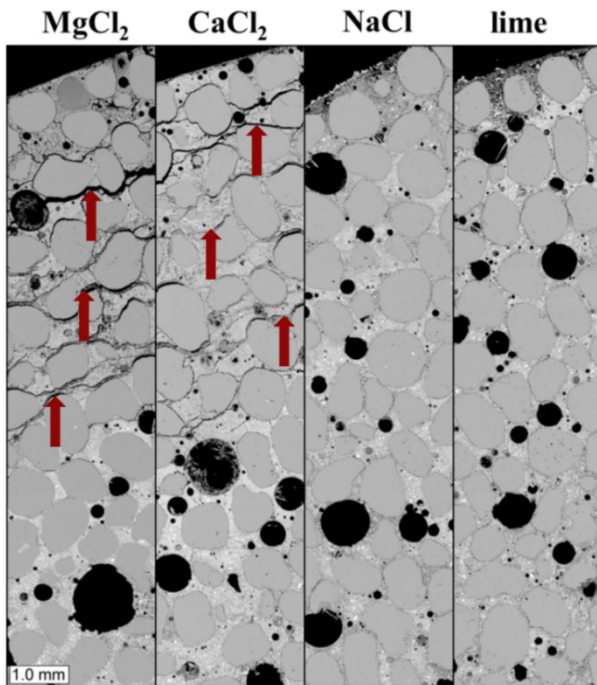


Figure 7. Backscatter electron micrographs of sections of mortar exposed to (a) MgCl_2 , (b) CaCl_2 , (c) NaCl , and (d) lime water. Cylinder edge exposed to solution is at the top. Note cracking (arrows) at the surface of samples soaked in MgCl_2 and CaCl_2 . No damage is observed in specimens soaked in NaCl or lime water (Sutter et al. 2008).

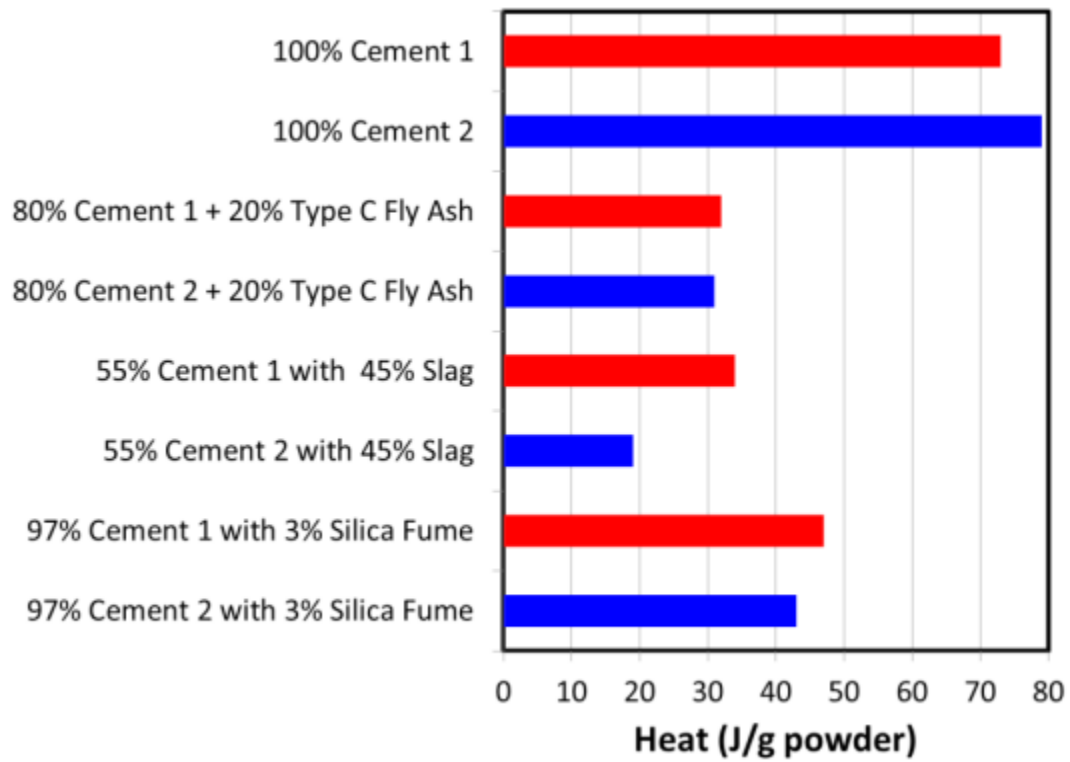
CURRENT RECOMMENDATIONS TO MITIGATE CHEMICAL DEICER DISTRESS

Guidance to address conventional physical freeze-thaw deterioration in the presence of deicers, including scaling, is well-documented (Kosmatka and Wilson 2016; ACI 2016) and described in an FHWA Tech Brief (Van Dam 2016). Recommendations include the use of a relatively low w/cm (0.45 or lower), entrainment of an air-void system capable of relieving osmotic and hydraulic stresses generated as ice forms, good finishing practices so that the w/cm and the entrained air-void system is not altered at the surface, and adequate curing to support cement hydration. To avoid physical freeze-thaw damage at joint locations, it is essential that the concrete does not become critically saturated. This occurrence can be minimized through design, construction, and maintenance strategies that (1) reduce the ingress of water-salt solutions into joints, and (2) quickly drain these solutions from the joint. These steps will help avoid critical saturation of the concrete that would lead to freeze-thaw damage in even a few cycles.

Recommendations for addressing chemical deicer distress are still under development, but research has focused on the need to (1) reduce the amount of calcium hydroxide present in the HCP, or (2) decrease the access of salt solution into the concrete. The use of supplementary cementitious materials (SCMs) will reduce the amount of calcium hydroxide in the HCP as well as decrease the permeability of the concrete, thereby reducing salt solution ingress. The ability of SCMs to reduce calcium hydroxide is partially due to dilution, in which the portland cement is replaced by SCMs, and partially by the consumption of calcium hydroxide through the pozzolanic reaction that occurs with certain SCMs (e.g., fly ash, slag cement and silica fume). Reducing calcium hydroxide results directly in a reduction in the formation of calcium oxychloride, as illustrated in figure 8, which also illustrates that cement source/composition influences the amount of calcium oxychloride that forms (Weiss and Farnam 2015).

Another method for reducing salt solution ingress is through some type of barrier. Research has suggested that the application of certain penetrating sealants (i.e., certain silanes, siloxanes, soy methyl ester polystyrene, and others) directly to concrete joints may provide a barrier to the ingress of chemical deicers and offer some level of protection (Sutter et al. 2008; Weiss and Farnam 2015). Laboratory studies and field test site monitoring are underway to determine the efficacy of this strategy.

AASHTO PP-84 (AASHTO 2017) describes a test method based on low-temperature differential scanning calorimeter (LT-DSC) that can be used to evaluate the potential reactivity of HCP and a salt solution by measuring the heat associated with calcium oxychloride formation (Weiss and Farnam 2015; Monical et al. 2016). If proven reliable, this method will provide a method for optimizing the composition of the cementitious materials by minimizing the potential for formation of calcium oxychloride. It will be possible to test specific portland cement and SCM systems, making this a practical screening tool for selecting materials for use under anticipated deicing conditions.



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Figure 8. Heat release associated with the formation of calcium oxychloride during low-temperature differential scanning calorimetry for different cementitious systems (Weiss and Farnam 2015).

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