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The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete

Study SD2002-01
Implementation Guide

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16. Abstract <p>This research project investigated the effects of concentrated brines of magnesium chloride, calcium chloride, sodium chloride, and calcium magnesium acetate on portland cement concrete. Although known to be effective at deicing and anti-icing, the deleterious effects these chemicals may have on concrete have not been well documented. As a result of this research, it was determined that there is significant evidence that magnesium chloride and calcium chloride chemically interact with hardened portland cement paste in concrete resulting in expansive cracking, increased permeability, and a significant loss in compressive strength. Although the same effects were not seen with sodium chloride brines, it was shown that sodium chloride brines have the highest rate of ingress into hardened concrete. This latter fact is significant with respect to corrosion of embedded steel. The mechanism for attack of hardened cement paste varies with deicer chemical but in general, a chemical reaction between chlorides and cement hydration products results in the dissolution of the hardened cement paste and formation of oxychloride phases, which are expansive. The chemical attack of the hardened cement paste is significantly reduced if supplementary cementitious materials are included in the concrete mixture. Both coal fly ash and ground granulated blast furnace slag were found to be effective at mitigating the chemical attack caused by the deicers tested. In the tests performed, ground granulated blast furnace slag performed better as a mitigation strategy as compared to coal fly ash. Additionally, siloxane and silane sealants were effective at slowing the ingress of deicing chemicals into the concrete and thereby reducing the observed distress. In general, the siloxane sealant appeared to be more effective than the silane, but both were effective and should be considered as a maintenance strategy.</p>					
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TABLE OF ACRONYMS

Acronym	Definition
AASHTO	American Association of State Highway and Transportation Officials
ACI	American Concrete Institute
ACR	Alkali Carbonate Reaction
ASTM	American Society for Testing and Materials
CaCl ₂	Calcium Chloride
CMA	Calcium Magnesium Acetate
GGBFS	Ground Granulated Blast Furnace Slag
MgCl ₂	Magnesium Chloride
NaCl	Sodium Chloride
NCHRP	National Cooperative Highway Research Program
PCA	Portland Cement Association
RCPT	Rapid Chloride Permeability Test
RGB	Red-Green-Blue
RWIS	Road Weather Information Systems
SCM	Supplementary Cementitious Materials
w/cm	Water-to-Cementitious Material Ratio

INTRODUCTION

The use of various chemicals for snow and ice control is an integral part of the winter maintenance activities of most transportation agencies. Although the use of “road salt” and other deicing materials can be traced back to some of the earliest days of paved roadways, the application of these materials became more widespread, and their need more acute, with the dawning of the Interstate era in the mid-1950s.

In the last few decades, implementation of new snow and ice control strategies have been implemented, as well as the introduction of new chemicals. For example, many agencies now employ both “anti-icing” and “deicing” strategies, in which anti-icing is defined as any treatment applied prior to ice formation to eliminate ice accumulation or facilitate its removal, and deicing is defined as any effort to remove ice from roads or bridges after deposition on the surface (Sutter 2008). For the purpose of this document, the generic term “deicing chemical” or “deicer” will be used to refer to materials that are applied to concrete for either anti-icing or deicing strategies.

Although conventional road salt (NaCl) historically has seen the greatest use on transportation facilities, a number of different materials are used for snow and ice control. Among the most common materials are (Levelton 2007):

- Chloride salts, including sodium chloride, calcium chloride, and magnesium chloride.
- Organic products, including calcium magnesium acetate, potassium acetate, and glycols.
- Nitrogen products, such as urea.
- Abrasives, such as sand and cinders. (note: these are often applied alone or in combination with deicers as a traction aid.)

As illustrated in Figure 1, when added to water, deicing chemicals reduce the freezing point of the solution below the freezing point of the water alone. Chloride salts, for example, react with moisture to create a layer of salty water (i.e. brine) that has a freezing point below 32°F [0°C], helping to break the bond between the ice and the road surface allowing the resulting mixture to be plowed from the road. Table 1 summarizes some of the characteristics of these materials.

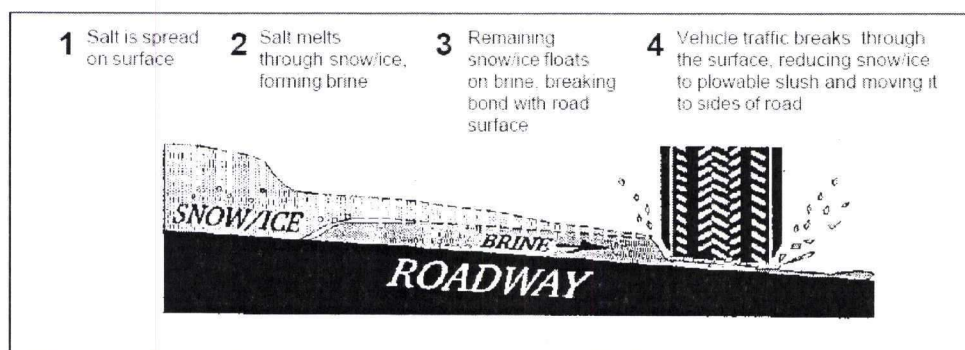


Figure 1. Snow and ice control with deicing chemicals (TAC 1999)

Table 1. Properties of common snow and ice control materials (adapted from Levelton 2007)

Material	Chemical Formula	Forms Used	Effective Min. Temp. °F [°C]	Median Cost per Ton
Sodium Chloride	NaCl	Primarily solid, but increasing use of liquid	14 [-10]	\$36
Calcium Chloride	CaCl ₂	Mostly liquid brine; some solid flake	-24 [-31.1]	\$120
Magnesium Chloride	MgCl ₂	Mostly liquid brine; some solid flake	5 [-15]	\$95
Calcium Magnesium Acetate	[Ca Mg ₂ (C ₂ H ₃ O ₂) ₂] ₆	Mostly liquid and some solid	23 to 27 [-5 to -2.8]	\$1,280
Potassium Acetate	KC ₂ H ₃ O ₂	Liquid only	-76 to -22 [-60 to -30]	n/a
Glycols	C ₃ H ₈ O ₂ , C ₂ H ₆ O ₂	Liquid only		n/a
Urea	(NH ₂) ₂ CO	Mostly solid	19 to 25 [-7.2 to -3.9]	n/a

The chloride salts listed in Table 1 have been commonly used on street and highway pavements and offer many advantages including their low cost and relative effectiveness as a snow and ice control chemical. Unfortunately, these materials also have several disadvantages including their environmental impacts on vegetation, groundwater, wildlife, their corrosive effects on vehicles, and deleterious effects on concrete infrastructure. While these disadvantages are not enough to fully deter their use, they are sufficient to advocate the conscientious and effective use of these materials.

The organic and nitrogen products listed in Table 1 (i.e. acetates, glycols, and urea) are commonly used on airfield pavements because of concerns about the corrosive effects of chlorides on aircraft. While these materials have demonstrated adequate snow and ice fighting ability, some are very expensive (e.g. acetates), others may have adverse environmental effects (e.g. glycols, urea), and still others have been linked to severe and deleterious effects on concrete (e.g. potassium acetate).

The Federal Highway Administration (Ketcham et al. 1996), the Transportation Association of Canada (TAC 1999; TAC 2003), and a recent National Cooperative Highway Research Program (NCHRP) report (Levelton 2007) all provide recommendations and guidance on snow and ice control activities, managing deicing chemicals, and selecting appropriate materials. While informative, those documents do not provide extensive information on dealing with the potential chemical effects of deicing chemicals on concrete. As a result, these guidelines - drawing upon the information from a number of technical sources - have been prepared to provide technical guidance to design engineers, material producers and suppliers, construction personnel, contractors, and maintenance personnel on ways of preventing or minimizing the effects of deicing chemicals on concrete pavements. The guidelines begin with a quick overview of the mechanisms that can induce distresses in concrete pavements, and then presents strategy guidelines in three specific areas: durable concrete mix, concrete construction, and post-construction mitigation measures.

CONCRETE DETERIORATION IN THE PRESENCE OF DEICING CHEMICALS

There are two general forms of deterioration that can occur when concrete is exposed to high concentrations of chloride-based deicing chemicals. The first is a degradation of the concrete itself and the second is the corrosion of embedded steel leading to deterioration of the concrete. The mechanisms for each of these forms of deterioration are briefly described in the following sections.

CONCRETE DEGRADATION

Degradation of concrete as a result of exposure to deicing chemicals occurs as the result of physical and chemical mechanisms. Physical mechanisms associated with the repeated application of deicing chemicals lead to scaling or crazing of the slab surface (Van Dam et al. 2002). The primary mechanisms considered are not exactly known, but likely involve a combination of increased saturation, thermal stresses generated when a deicer melts ice, and increased osmotic pressures induced as the deicer imbalances the ionic concentration in the capillary pore solution in the concrete (Mindess et al. 2003; Pigeon and Plateau 1995). Deicer scaling/deterioration is more likely to occur in concrete that has been over-vibrated or improperly finished, actions that create a weak layer of paste or mortar either at or just below the surface (Mindess et al. 2003). This weakened layer is more susceptible to damage incurred due to stress generated by the application of deicers. However, even adequately properly finished concrete can be susceptible to the development of salt scaling if it possesses inadequate entrained air and/or is of poor quality. Figure 2 shows scaling of a concrete slab.



Figure 2. Concrete scaling caused by deicing chemicals (Sutter 2008)

Recent studies indicate that chemical alteration of the cement paste can also occur, resulting in dissolution of calcium hydroxide, coarsening of the concrete pore system and the formation of deleteriously expansive oxychloride compounds (Sutter 2008). This latter distress mechanism was identified when concrete laboratory specimens were exposed to concentrated solutions of calcium chloride or magnesium chloride. The solution strengths used in the referenced study were approximately 30-50% lower than the typical application strength of solutions used for anti-icing or deicing (Sutter 2008). Besides significant expansion and cracking, a significant loss in strength and degradation in freeze-thaw performance were also identified (Sutter 2008). In the same study, chemical deterioration of concrete was not found in, or was not indicated in, specimens exposed to highly concentrated NaCl solutions.

Potassium acetate has been linked to deterioration that is similar to alkali-silica reactivity (ASR) distress in concrete (Rangaraju, Sompura, and Olek 2006). Although still the subject of considerable research, current evidence suggests that an adverse reaction occurs between the potassium acetate and the calcium hydroxide present in the hydrated cement paste, which results in a dramatic increase in the pH of the concrete pore solution (from a pH 11 to approximately pH 15)¹. This “pH jump” can trigger ASR if susceptible aggregates are present.

CORROSION OF EMBEDDED STEEL

Corrosion of embedded steel appears as rust colored staining, spalling, cracking, and associated deterioration of the concrete above or surrounding the areas affected by active corrosion as shown in Figure 3. Although steel embedded in concrete forms a thin passivity layer of oxide providing protection from reaction with oxygen and water, this passivity film can be easily broken down under the action of chloride ions (Neville 1996). The soluble chloride ion level at which steel reinforcement corrosion begins in concrete is about 0.2 to 0.4 percent by mass of cement (Kosmatka, Kerkhoff, and Panarese 2002). In most transportation structures, the primary source of the chloride ions is from the application of deicing salts, although it can also come from other sources such as seawater or the presence of a calcium chloride accelerator in the concrete mix (Van Dam et al. 2002).

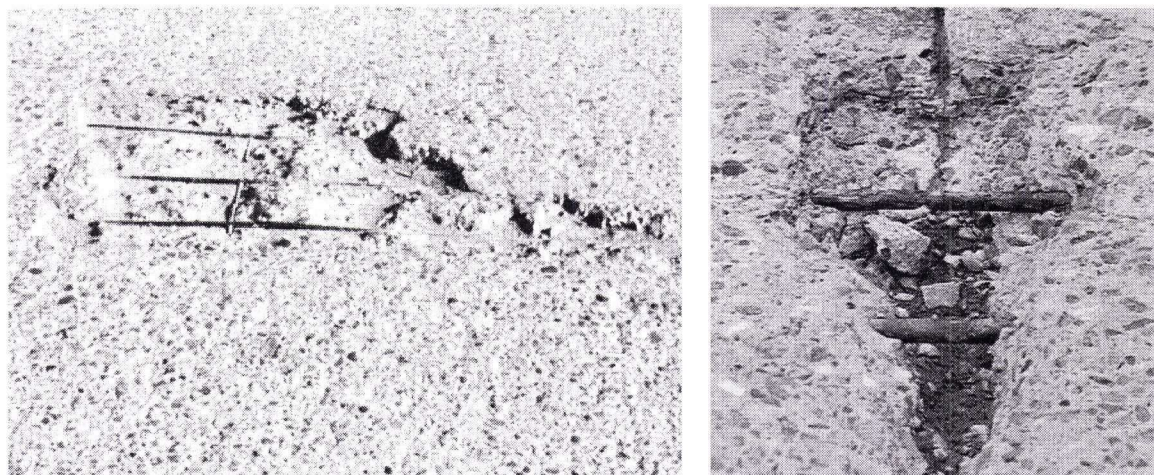


Figure 3. Corrosion of high steel (left photo) and of embedded dowel bars (right photo)

STRATEGIES FOR MINIMIZING EFFECTS OF DEICERS ON CONCRETE PAVEMENT

Deicing chemicals have the potential to create significant damage and deterioration to concrete structures. However, there are a number of strategies that can be employed to help minimize their deleterious effects. These strategies are described in the following sections.

¹ The usual range of pH values encountered is between 0 and 14, with 0 being the value for concentrated hydrochloric acid (1 M HCl), 7 the value for pure water (neutral pH), and 14 being the value for concentrated sodium hydroxide (1 M NaOH). It is possible to get a pH of -1 with 10 M HCl, but that is about the practical limit of acidity. At the other extreme, a 10 M solution of NaOH would have a pH of 15. (<http://hyperphysics.phy-astr.gsu.edu/HBASE/Chemical/ph.html>)

DURABLE CONCRETE MIX

The first and foremost strategy for eliminating or reducing the adverse effects of deicing chemicals is the development of a durable concrete mix. Durability is defined as the ability of concrete to resist weathering action, chemical attack, abrasion, or any other process of deterioration (ACI 2001). Inherent in this definition is that different concretes may be exposed to different environmental forces, suggesting that different concrete mixes are required to maintain the same level of durability for different conditions.

Durability in and of itself is not an intrinsic property of the concrete, but rather the sum total of all of the factors that are part of the concrete production process and the environment in which the structure serves. This includes constituent materials, mix proportioning, and construction as well as the climatic conditions and external exposure to potentially harmful materials. By adopting a more holistic approach in which the entire concrete structure is viewed as a system, more durable concrete will result (Van Dam et al. 2002).

The permeability of the concrete is a key property contributing to concrete durability, and plays an important role in determining the effects of deicing chemicals on the degradation of the concrete and the corrosion of embedded steel. A denser concrete material, or in other words less permeable, has greater capability to resist the ingress of chemicals and their accompanying deleterious effects.

Permeability is defined as the ease with which fluids can penetrate concrete, and should not be confused with porosity, which is a measure of the number of voids in concrete (Taylor et al. 2006). Permeability can be reduced by minimizing voids and cracks, ensuring a good bond between the aggregate and cementitious paste, minimizing the porosity of the paste, and minimizing the paste fraction in the concrete (Leek, Harper, and Ecob 1995). Mehta (1997) states that it is desirable from the perspective of durability to maximize the aggregate content and minimize the paste content to promote the water-tightness of the concrete. At the same time, other critical aspects of a durable concrete mix cannot be ignored such as the use of durable aggregates, maintaining necessary strength or workability, or the development of an effective air-void system.

Detailed information on the production of durable concrete is provided in a number of documents (for example, Pigeon and Plateau 1995; ACI 1991; ACI 2001; Kosmatka, Kerkhoff, and Panarese 2002; Van Dam et al. 2002; Taylor et al. 2006). Some general guidelines are provided in the following sections. A thorough mix design analysis and the preparation of trial mixes using project-specific materials is strongly recommended to ensure that the resultant mixture exhibits the required durability, strength, and workability characteristics for the application. Mix proportioning procedures are available from both the PCA and the ACI (Kosmatka, Kerkhoff, and Panarese 2002 and ACI 1991, respectively).

Cement

In order to minimize the scaling of concrete exposed to severe freeze-thaw, deicer, and sulfate exposures, some sources recommend a minimum cement content of 564 lb/yd³ [335 kg/m³] (Kosmatka, Kerkhoff, and Panarese 2002). These sources indicate that lean concrete (with cement contents of 405 lb/yd³ [240 kg/m³] or less) are particularly vulnerable to deicer scaling. Other references state that a minimum cement content is not necessary as long as the concrete can be easily placed and has sufficient strength, low permeability, and an adequate air-void system to protect it against paste freeze-thaw damage (TRB 1999; Taylor et al 2006).

Supplementary Cementitious Materials

Supplementary cementitious materials (SCMs), which include materials such as fly ash, ground granulated blast furnace slag (GGBFS), and silica fume, are often used in concrete mixtures to enhance durability. As the name implies, some SCMs have cementitious properties on their own that contribute to strength development in concrete by undergoing hydration and forming hydration products similar to those formed through the hydration of portland cement. Other SCMs are almost entirely pozzolanic, which means that they react with calcium hydroxide produced through cement hydration to form calcium-silicate-hydrate, a very desirable hydration product. This latter property can provide an effective way of minimizing the effects of chemical attacks involving calcium hydroxide (e.g. alkali-silica reaction or ASR, deicer attack), as it reduces the amount of soluble calcium hydroxide in the hardened cement paste (TRB 1999, Sutter 2008), which in turn reduces the hydroxide ion available to react. Because of their very fine particle size, these materials also act as “micro-aggregate,” packing into and filling spaces that would otherwise be left empty (Van Dam et al. 2002). This not only improves workability and reduces the water demand of the fresh concrete, but it also produces a denser, significantly less permeable microstructure.

Concrete mixtures made with SCMs have exhibited variable performance with respect to deicer scaling resistance. Often poor performance of concrete mixtures that include SCMs can be traced to improper curing. Generally, these mixtures require longer times to achieve ultimate strength and permeability because the pozzolanic reaction is much slower than is the normal hydration reactions between portland cement and water. When partially cured concrete is exposed to deicers, physical attack leading to scaling can occur because the cement paste is not strong enough to resist the forces causing scaling. Likewise, partially cured concrete is more permeable and therefore ingress of chemicals increases and the associated chemical interactions with either the concrete or embedded steel is accelerated (Sutter 2008). The ACI 318 building code states the maximum dosage of fly ash and GGBFS should be 25 and 50 percent by mass of the cementing materials, respectively (Kosmatka, Kerkhoff, and Panarese 2002). Actual dosage rates must be established for the specific materials being used based on the specific application. Ultimately, the use of SCMs is a good way to achieve deicer attack protection in terms of decreasing the concrete permeability.

Water

Acceptance criteria for mixing water used in the production of concrete are given in AASHTO T26. In general, the water should be relatively free of chlorides, sulfates, alkalis, and other potential contaminants or impurities.

Water-to-Cementitious Ratio

According to ACI, a maximum water-to-cementitious material ratio (w/cm) of 0.40 to 0.45 should be used in the mix proportioning, depending on exposure conditions (ACI 201). The w/cm is the mass of the water in the mix divided by the mass of cementitious materials (portland cement + supplementary cementitious materials). The w/cm selected for a mix design must be the lowest value required to meet anticipated exposure conditions, with recommended values as follows (Kosmatka, Kerkhoff, and Panarese 2002):

- Concrete exposed to freezing and thawing in a moist condition or deicers: ≤ 0.45
- For corrosion protection for reinforced concrete exposed to deicers: ≤ 0.40 (unless an additional 0.5 inch [12.5 mm] of concrete cover is added).

Some agencies specify even lower w/cm values for high performance concrete.

In general, a lower w/cm results in a less permeable concrete. Therefore, it is widely accepted that a lower w/cm results in better protection from deicer attack. However, the recent study by Sutter (2008) indicates that lower w/cm mixtures do not perform better than mixtures with a higher w/cm with regards to chemical attack by deicers. In fact, there was strong evidence that the lower w/cm perform worse. Therefore, it is not recommended that a reduced permeability be achieved by means of lowering the w/cm alone. The use of SCMs is recommended as a first choice for effecting concrete permeability. Additional research is needed to confirm the observations reported by Sutter (2008).

Aggregates

Strong and durable aggregates should be used that are not reactive or susceptible to freeze-thaw or moisture damage. Such aggregates should have a proven track record of acceptable performance or should meet the requirements ASTM C295 (*Standard Guide for Petrographic Examination of Aggregates for Concrete*) to characterize the physical and chemical properties of the aggregate, with supplemental laboratory testing conducted to further define the physical and chemical stability of the aggregate (Van Dam et al. 2002).

An effective aggregate gradation should be employed, one that uses the largest nominal maximum size that is practical for job conditions (Taylor et al 2006; Kosmatka, Kerkhoff, and Panarese 2002). The use of larger maximum aggregate size minimizes void space and paste requirements, which helps control shrinkage. For pavements, both ACI and PCA recommend that the maximum aggregate size should be less than one-third the slab thickness and three-quarters of the free space between reinforcing bars or reinforcing bars and formwork (ACI 1991; Kosmatka, Kerkhoff, and Panarese 2002). Although the use of 0.75- to 1.0-inch [19 to 25.4 mm] top sizes is commonly used by highway agencies, several agencies are returning to the use of larger (1.5 to 2 inch [38 to 51 mm]) maximum coarse aggregate sizes.

Traditionally, gap-graded aggregate mixtures have been used in the production of concrete, in which coarse aggregates (particle sizes greater than 3/16 inch [4.75 mm]) are combined with fine aggregates (smaller than 3/16 inch [4.75 mm]). This often leaves a gap in the intermediate-sized aggregate around the 3/8 inch [9.5 mm] size, which may make the resultant mixture more susceptible to segregation and shrinkage, and may exhibit poor workability and placeability. The use of well-graded aggregates that contain a balanced variety of sizes are expected to help maximize the aggregate volume, reduce shrinkage and permeability, and enhance workability (Shilstone 1990; Taylor et al 2006).

Air-Void System

An effective air-void system is needed to protect the hardened concrete from freeze-thaw damage and deicer scaling (Van Dam et al. 2002). An air-void system is established using air entraining agents that create small, stable air voids in the hardened concrete that serve as “relief valves” to dispel osmotic and hydraulic pressures caused by water freezing in the capillaries and pores of the cement paste (Kosmatka, Kerkhoff, and Panarese 2002). Typical entrained air contents for concrete mixes range from about 4 to 8 percent, and are dependent upon the severity of the environmental exposure and the nominal maximum coarse aggregate size as shown in Table 2.

Table 2. Recommended total air contents (Kosmatka, Kerkhoff, and Panarese 2002)

Nominal Maximum Size Aggregate, inch [mm]	Average Air Content, Volume Percent ¹		
	Severe Exposure ²	Moderate Exposure ³	Mild Exposure ⁴
< 3/8 [9.5]	9	7	5
3/8 [9.5]	7.5	6	4.5
1/2 [12.5]	7	5.5	4
3/4 [19.0]	6	5	3.5
1 [25.0]	6	4.5	3
1-1/2 [37.5]	5.5	4.5	2.5
2 ⁵ [50]	5	4	2
3 ⁵ [75]	4.5	3.5	1.5

¹ Project specifications often allow the air content of the concrete to be within -1 to +2 percentage points of the table target values.
² Concrete exposed to wet-freeze-thaw conditions, deicers, or other aggressive agents.
³ Concrete exposed to freezing but not continually moist, and not in contact with deicers or aggressive chemicals.
⁴ Concrete not exposed to freezing conditions, deicers, or aggressive agents.
⁵ These air contents apply to the total mix, as for the preceding aggregate sizes. When testing these concretes, however, aggregate larger than 1-1/2 inch [37.5 mm] is removed by handpicking or sieving and the air content is determined on the minus 1-1/2 inch [37.5 mm] fraction of mix. (Tolerance on air content as delivered applied to this value.)

However, it is not the total air content that is important to the durability of the mix, but rather the distribution of the air voids within the concrete microstructure; it is generally desired that the average distance between any point in the paste and an air void, referred to as the “spacing factor” and designated as \bar{L} , be less than 0.008 in [0.2 mm] (Kosmatka, Kerkhoff, and Panarese 2002; Taylor et al. 2006). The concept of the spacing factor is shown in Figure 4.

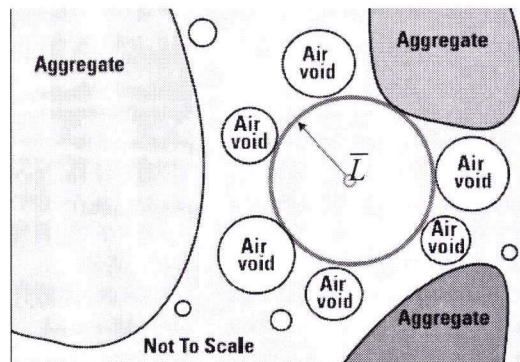


Figure 4. Air-void spacing factor (Taylor et al. 2006)

Admixtures

Accelerating admixtures are commonly added to a concrete mix in order to achieve high early strength, but the most common accelerating admixture—calcium chloride, a commonly used deicing chemical—is known to promote corrosion of embedded steel, and may have other negative effects on concrete durability, including increasing drying shrinkage and adversely affecting the pore structure (Van Dam et al. 2005). If these issues are a concern, then non-chloride accelerators should be used.

Water-reducing admixtures may be added to concrete mixtures to reduce the amount of water required to produce concrete of a given consistency. Reductions of 5 to 10 percent are common, allowing the

use of a lower w/cm while maintaining a desired slump, and having the beneficial effect of increasing strength and reducing permeability (Van Dam et al. 2002). Even greater reductions in water can be achieved through the use of mid-range and high-range water-reducing admixtures.

Corrosion inhibitors may be added to concrete used in parking structures, marine structures, and bridges that are exposed to chloride salts. These admixtures react chemically to either block the corrosion reaction of the chloride ions with the steel (anodic inhibitors) or by reacting with the steel surface to interfere with the reduction of oxygen (cathodic inhibitors) (Kosmatka, Kerkhoff, and Panarese 2002). Common corrosion inhibitors include calcium nitrite, sodium nitrite, and phosphates. Corrosion inhibitors are relatively expensive, increasing the cost of a concrete structure by approximately 8 percent (Mehta 1997).

Laboratory Tests

Two tests are available that can assist in evaluating the capabilities of concrete to resist deicer scaling and corrosion of embedded steel. These tests are described below:

- ASTM C672, *Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals*. This test method ponds the top surfaces of concrete specimens with a standard solution of calcium chloride and water or other chemical deicers and subjects the specimens to a series of freeze-thaw cycles. The condition of the surface is monitored during the cycling period and qualitative assessments of the scaling are made. Up to 50 cycles or more may be required to adequately assess the scaling, a process that can take 10 weeks or longer.
- ASTM C1202, *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*. This test method is sometimes referred to as the "rapid chloride" penetration test (RCPT), and is also covered under AASHTO T 277. This test was developed as rapid way of assessing the potential susceptibility of a concrete sample to chloride penetration, as compared to conventional "ponding" tests that can take several months to complete. The "rapid chloride" test measures the electrical conductivity of a concrete specimen, which is used as a surrogate indicator for the permeability of the concrete. The output of the test is a measure of the electrical charge passed through the sample, expressed in coulombs. The test is not intended to provide exact measures of the charge passed, but rather provides a way of comparing the relative resistivity of different samples, using the guidelines provided in Table 3. Users of the test are cautioned that several factors may affect the test results. As an example most concretes, if properly cured, become less permeable with time and therefore the age of the concrete specimen can affect the test. As other examples, the inclusion of certain admixtures such as calcium nitrite, may adversely affect results and the presence of reinforcing steel may affect the conductivity of the sample.

Table 3. Chloride permeability based on charge passed

Charge Passed (Coulombs)	Chloride Permeability
>4,000	High
2,000 – 4,000	Moderate
1,000 – 2,000	Low
100 – 1,000	Very Low
< 100	Negligible

These two tests are most commonly used for assessing the potential for deicer scaling and chloride permeability, although a number of other tests are sometimes used (e.g., AASHTO T 260 *Standard Method of Test for Sampling and Testing Chloride Ion in Concrete and Concrete Raw Materials*, AASHTO T 259 *Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration*, ASTM C1152 *Test Method for Determining the Apparent Bulk Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion*). These tests should be considered along with recommended mix design guidelines in order to develop a durable concrete mixture. A summary of a broad range of concrete tests is provided by Taylor et al. 2006.

EFFECTIVE CONCRETE CONSTRUCTION

Effective construction practices are essential to the long-term performance of concrete structures. Even a well-designed concrete structure will not provide its expected level of service if it is poorly constructed. Moreover, the need for effective construction becomes even more acute when the concrete structure will be exposed to severe or adverse conditions.

Durable concrete, as described in the previous section, should use non-reactive materials constructed in a dense and relatively impermeable matrix. From a construction standpoint, there are a number of factors that can affect this outcome, from the ambient and seasonal construction conditions to the placement and consolidation efforts, to the finishing and curing practices. Some of these key construction factors are described in the following sections.

Weather Management

Guidelines on hot- and cold-weather paving are summarized in Tables 4 and 5. Placement of concrete under extreme weather conditions can be detrimental to the development of durable concrete.

Table 4. Hot weather paving recommendations (adapted from Kohn et al. 2003)

1. Do not exceed the maximum allowable *w/cm* ratio or the manufacturer's maximum recommended dosage of any admixture.
2. Retarding admixtures may be used if their performance has been verified during trial batches.
3. The substitution of slag, Class F fly ash, or natural pozzolans for part of the cement may be an option.
4. Class C fly ashes with high contents of Al_2O_3 may cause problems associated with premature stiffening.
5. Air contents can be corrected by increasing the dosage of air entraining admixture.
6. Early age thermal cracking may be prevented by ensuring that the temperature of the plastic concrete is as low as practical. It should not exceed 90°F [32.2°C].
7. Avoid the use of hot cement or fly ash provided by the supplier.
8. Mixing water may be chilled, or chipped ice may be used in substitution for some of the water.
9. Mixing and transporting equipment may be painted white or a light color to minimize the heat absorbed from the sun.
10. Schedule concrete placements for nighttime.
11. The base should be moistened before the concrete is placed to keep the temperature down and to keep it from absorbing water from the concrete.
12. The concrete should be placed and finished as rapidly as possible and curing compound applied at the earliest possible time. The use of a white curing compound will reflect the sun's heat.
13. Steps should be taken during hot weather to reduce the rate of evaporation from the concrete. The rate of evaporation is a function of air temperature, concrete temperature, relative humidity, and wind speed. When the rate of evaporation is predicted to be above 0.2 lb/ft²/hr [0.98 kg/m²/hr], provide fog spraying or use an approved evaporation retardant as appropriate.
14. If conditions of temperature, relative humidity, and wind are too severe to prevent plastic shrinkage cracking, or corrective measures are not effective, paving operations must be stopped until weather conditions improve.

Table 5. Cold weather paving recommendations (adapted from Kohn et al. 2003)

1. Concrete mixture designs developed for placement at cooler temperatures normally have higher cement content than those used in hot weather.
2. The use of slag, fly ash, and pozzolans should be reduced or eliminated unless they are required to control alkali-silica reaction or to provide some degree of resistance to sulfate attack. In the later case, the total cementitious materials content may need to be increased, or the cement changed to Type III instead of Type I/II.
3. The required dosage of air entraining admixture should be lower than the dose at normal temperatures.
4. Because the concrete will take longer to set, there is also some danger of plastic shrinkage cracking, especially if the concrete is much warmer than the ambient air or if the wind is blowing.
5. An accelerating admixture conforming to ASTM C494 Type C or E may be used, provided its performance has been previously verified by trial batches.
6. Do not use admixtures containing added chlorides. Also, do not use calcium chloride.
7. Aggregates must be free of ice, snow, and frozen lumps before being placed in the mixer.
8. The temperature of the mixed concrete should not be less than 50 °F [10°C].
9. Concrete should not be placed when the temperatures of the air at the site or the surfaces on which the concrete is to be placed are less than 40 °F [4.4°C].
10. Covering and other means of protecting the concrete from freezing must be available before starting placement.
11. The concrete temperature should be maintained at 50 °F [10°C] or above for at least 72 hours after placement and at a temperature above freezing for the remainder of the curing time (when the concrete attains a compressive strength of 3,000 lb/in² [20.6 kPa]).
12. Corners and edges are the most vulnerable to freezing. Completely remove and replace any concrete that is damaged by freezing.

Contractors should have weather management plans in place to deal with such conditions, particularly hot- and cold-weather paving. Potential problems associated with hot-weather paving include rapid slump loss, reduced air contents, premature stiffening, plastic shrinkage cracking, and thermal cracking, whereas potential problems associated with cold-weather paving include delayed set time, slower rate of strength gain, and potential for early age cracking because of delays in sawcutting (Kohn et al. 2003).

The occurrence of untimely rain events may also cause problems during paving, such as washing away or diluting the paste at the surface. If a rainfall event occurs during paving, the contractor should halt paving operations immediately and cover the freshly placed concrete. No attempts should be made to remove any excess water on the surface, as this actually serves to work the water into the surface paste making it more vulnerable to scaling (Kohn et al. 2003). Rain-damaged concrete—if significant—can be addressed through diamond grinding of the concrete surface.

Consolidation

The goal of consolidation is to effectively remove entrapped air from the concrete system so that a dense and uniform concrete mixture results. For most structures greater than 3 inches thick, a combination of both external and internal vibration is needed to ensure adequate consolidation. External vibration is produced by vibratory rollers or screeds on the surface of the concrete, whereas internal vibration is applied through hand-operated spud vibrators or immersion-type vibrators mounted on a paver.

Effective vibration is essential to achieving a well-consolidated concrete mixture, but over vibration can lead to a number of undesirable effects, such as segregation of the mix and the disruption of the entrained air-void system. When using hand-held vibrators, these devices should be inserted into the mix at an angle to the concrete surface and should not be used to move concrete laterally as this could cause segregation. Furthermore, they should not be allowed to vibrate in a fixed position for an excessively long period of time.

In slip-form paving operations, illustrated in Figure 5, a series of vibrators are mounted on the paver just after the strike-off. The contractor will establish a suitable vibrating frequency early in the project that, in combination with the paving rate and the mixture characteristics, will produce a well-consolidated mixture (Van Dam et al. 2002). Typically, a vibrator frequency of 5,000 to 8,000 vibrations per minute is satisfactory for most mixtures at vibrator speeds greater than 3 ft [0.9 m] per minute (Taylor et al. 2006). It is important to recognize that any changes in paving speed should also necessitate changes in vibrator frequency in order to avoid segregation problems and loss of entrained air.

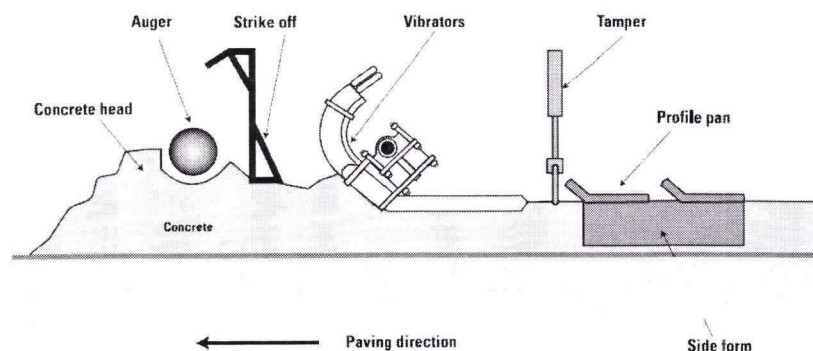


Figure 5. Schematic of slip-form paving machine showing location of vibrators (Taylor et al. 2006)

Embedded Steel

Embedded steel placed in concrete can include dowel bars and tie bars (located at joints) and reinforcing steel (located within the slab at various depths/positions). Dowel bars and tie bars are both placed at the mid-depth of the slab, with dowel bars providing positive load transfer across the joint

and tie bars holding joints tightly together and in vertical alignment. Reinforcing steel in a slab may be provided for crack control (to hold cracks tightly together) or, in structural concrete, may be designed to carry structural loading.

Embedded steel may be susceptible to corrosion in the presence of a chloride environment. Because dowel bars and tie bars are placed across a joint, they are especially susceptible to the ingress of both moisture and chloride ions. If significant corrosion of dowel bars occur, the transverse joint may “lock up” and can cause cracking or spalling at the joints; in advanced stages of corrosion, the effective diameter of the dowel bar or tie bar can be reduced, often to the point where load transfer or slab alignment may be lost. To combat the potential for corrosion, most dowel bars and tie bars are coated with a thin protective layer. Epoxy is the most commonly used protective coating, although a number of other materials have been used, such as plastic, stainless steel, or galvanization (Van Dam et al. 2002).

For reinforcing steel located within a slab, the provision of adequate cover is essential in order to prevent corrosion. The “cover” refers to the distance from the rebar to the surface of the concrete where chloride ions are present. An absolute minimum cover of 2 inches [51 mm] is required, with a design cover of 2.5 inches [63.5 mm] recommended in order to ensure adequate protection (Van Dam et al. 2002). The depth of cover can be measured using a pachometer, a small, magnetic detection device.

Finishing

After concrete placement, hand finishing may be needed to help embed large aggregate particles, fill any apparent voids, or correct small imperfections (Van Dam et al. 2002). Although it may be needed on some projects, hand finishing can lead to overworking of the surface that can work water to the surface and cause scaling. Moreover, if the hand finishing is done before the bleed water has disappeared, there is a greater chance of working the bleed water into the concrete, again affecting the durability of the near-surface concrete. Additional water should not be added to the concrete to assist in surface finishing.

In general, the need for hand finishing can be minimized by selecting a workable concrete mixture and properly operating the paving equipment (Kohn et al. 2003). If there is too great a need for hand finishing, then adjustments may be needed to the concrete mixture or to the paving operation.

Curing

Curing has long been recognized as an important step in constructing durable concrete pavements. The purpose of curing is to enhance hydration and strength gain by maintaining the moisture and temperature of the concrete immediately after placement and finishing (Kosmatka, Kerkhoff, and Panarese 2002). Adequate curing of the concrete is required to ensure that a durable pavement meeting specified strength requirements is obtained; inadequate curing can result in surface damage in the form of plastic shrinkage cracking, spalling, and erosion of the paste.

Over the years, a number of different curing methods and materials have been used, including ponding or fogging, wet burlap, plastic sheeting, and curing compounds. Some form of wet curing is considered most beneficial because it effectively maintains the presence of mixing water within the concrete. Unfortunately, for large paving projects such curing is not practical (time restrictions on many paving projects preclude the opportunity to conduct wet curing).

The application of liquid membrane-forming curing compound is the most commonly used method of curing. These are organic materials that form a skin over the surface of the concrete and help reduce

the loss of mixing water (typically limiting water evaporation to about 20 percent of that of unprotected concrete) (Taylor et al. 2006). Curing compounds are merely temporary coatings on the surface, and will break down and degrade with exposure to sunlight and traffic.

Liquid membrane-forming curing compounds are governed by ASTM C309 and AASHTO M 148. These materials can be either resin-based or wax-based, and may also be clear or white pigmented, with many agencies specifying white-pigmented, resin-based materials. However, products meeting these specifications can exhibit highly variable performance (Vandenbossche 1999), and it is suggested that agencies test curing compounds for their moisture-retention properties in accordance with ASTM C156. Some agencies have modified the ASTM C309 specification to incorporate more stringent requirements on the allowable moisture loss; Minnesota, for example, restricts the maximum allowable moisture loss to 0.08 lb/ft² [0.39 kg/m²] in 72 hours, compared to the 0.11 lb/ft² [0.54 kg/m²] value included in ASTM C309 (Vandenbossche 1999).

General guidelines on the use of curing compounds are provided below (Van Dam et al. 2002; Kohn et al. 2003; Poole 2005; Poole 2006; Taylor et al. 2006):

- Do not apply the curing compound to concrete that is still bleeding or has a visible sheen of water on the surface.
- Apply the curing compound immediately after texturing. Any delay, particularly during hot, windy conditions, can cause significant harm to the concrete resulting in plastic shrinkage cracking.
- Apply the curing compound uniformly to the concrete surface, ensuring that both the top of the slab and the sides are adequately covered as shown in Figure 6. For fixed form paving, the vertical edges should be coated after form removal. Automated equipment is more effective at providing uniform coverage, and hand-operated equipment should be used only on small areas.
- Recommended curing compound application rates are:
 - 200 ft²/gal [5 m²/l] for normal paving.
 - 150 ft²/gal [3.7 m²/l] for fast-track concrete.
 - 100 ft²/gal [2.5 m²/l] for thin slabs.

The application rates should be periodically checked by measuring the volume of curing compound applied to a given area and comparing that to the specified application rate.

- AASHTO recommends a 3-day curing period for pavements and a 7-day curing period for structures, including bridge decks (AASHTO 1998). The latter is increased to 10 days if more than 10 percent SCMs are included in the mix.

Drying Period

Newly placed concrete requires an absolute minimum of 30 days of environmental exposure before being subjected to deicing chemicals (Kosmatka, Kerkhoff, and Panarese 2002). Even longer periods are required if SCMs are being used. This will help add to the scaling resistance of the concrete. This requirement reveals the potential vulnerability of late season concrete construction, which may not have an adequate drying time before being exposed to deicers.

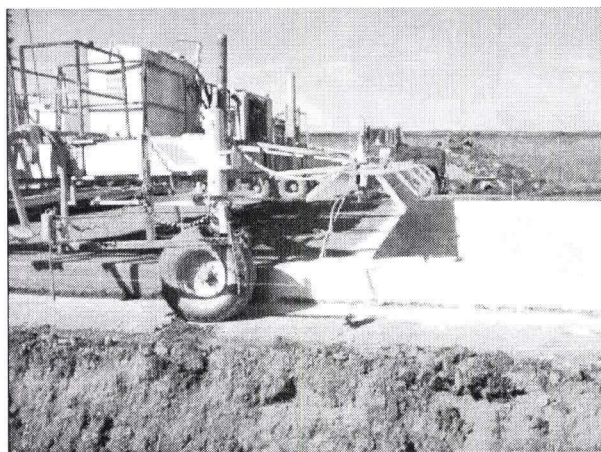


Figure 6. Uniform application of curing compound to slab surface and sides (Taylor et al. 2006)

POST-CONSTRUCTION MITIGATION MEASURES

Even when durable concrete has been produced and effectively constructed, there are a number of post-construction mitigation measures that can be taken to help further minimize the potential deleterious effects of deicing chemicals. Some of these recommended activities are described in the following sections.

Improved Winter Maintenance Practices

More agencies are developing formal winter maintenance plans that incorporate “best practices” for the application of deicing chemicals. This is part of a comprehensive approach that recognizes the external costs associated with the use of these chemicals, particularly as they apply to environmental effects including, among others, surface and groundwater contamination, vegetation damage, soil impacts (increased alkalinity and reduced permeability), and wildlife toxicity (Levelton 2007). In addition, there are societal costs associated with the use of deicing chemicals such as vehicle corrosion and infrastructure deterioration (Levelton 2007). All of these factors are positively affected by reducing the amount of deicing chemicals applied.

There are a number of initiatives currently being used or evaluated to reduce the amount of deicing chemicals used to maintain a safe, bare-pavement roadway including (TAC 1999):

- Reducing the accumulation of snow and ice on the road. Improved geometric designs and the installation of strategically placed snow fences are techniques that have been used to reduce the accumulation of snow on roadways.
- Predicting when to apply deicing chemicals. Advances in weather reporting technology and state-of-the-art Road Weather Information Systems (RWIS) provide up-to-the-minute information to winter maintenance crews so that better informed decisions can be made as to when the application of deicing chemicals may be needed.
- Improving the application of chemicals. Better distribution systems have greatly reduced waste by getting more of the material on the surface, and electronic spreader controls have provided a better understanding of the amount of deicing chemicals being used.

- Maximizing the effect of deicing chemicals. This includes a number of practices, such as pre-wetting the pavement with brine prior to the application of the solid deicer and allowing the material sufficient time to work before plowing and re-application.

Selection of Deicing Chemicals

The various deicing chemicals used in roadway winter maintenance can have different effects on the durability of the concrete, depending upon the chemical used and its concentration. Figure 7 shows the partial phase diagrams for mixtures of water and common deicing chemicals, showing the freezing point of a water-deicer solution as a function of the concentration of deicing chemical, in weight percent. Note that for all deicing chemical brines, a maximum freezing point is obtained at a specific concentration and exceeding that concentration only serves to increase the freezing temperature. This minimum in the solution freezing temperature is referred to as the eutectic temperature and the corresponding solution strength as the eutectic composition. By reducing the solution strength (i.e. concentration of deicing chemical) to less than the eutectic composition, higher freezing points result. When conditions permit, solution strengths should be reduced to achieve the lowest freezing point needed for the pavement and ambient temperatures.

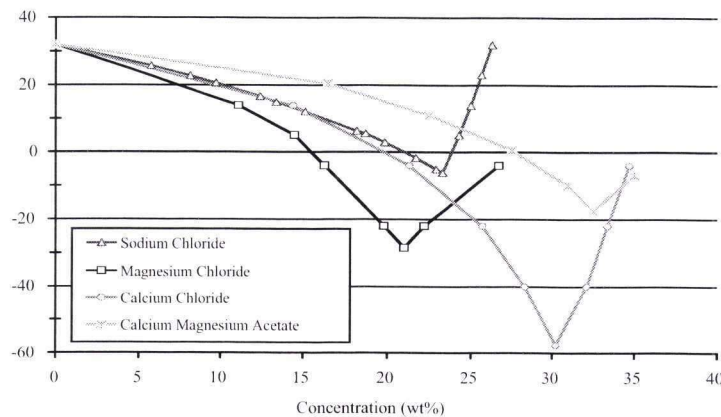


Figure 7. The partial phase diagrams for mixtures of water and common deicing chemicals. The freezing point of the water-deicer solution is plotted as a function of the concentration of deicing chemical, in weight percent. Note that for all deicing chemicals, a maximum freezing point is shown (Sutter 2008)

A publication by The Insurance Corporation of British Columbia (Keep 2000) provides tables of solution freezing point as a function of solution specific gravity. This provides a simple way of estimating the solution strength and freezing point of a salt brine solution. Reducing solution strength will also reduce salt use and therefore the cost of deicing operations.

The study by Sutter (2008) indicated that, regardless of the distress mechanism, reducing deicer solution concentrations reduces the magnitude of distress and distress progression rate. Thus, any effort to reduce deicer application concentrations or rates will result in less damage to concrete structures. It is also recommended that $MgCl_2$ and $CaCl_2$ should be applied with an initial concentration less than the pessimum level with respect to concrete deterioration (i.e., 20 percent for $MgCl_2$ and 22 percent for $CaCl_2$) (Sutter 2008).

Obviously there are significant trade-offs that must be weighed when selecting a deicer. It is important to keep in mind the negative effects of each chemical when making that selection, not just their

relative performance as a deicing chemical. The study by Sutter (2008) indicated that NaCl brines have a minimal effect on hydrated cement paste; whereas a clear mechanism for chemical attack of hydrated cement paste in concrete was shown for the $MgCl_2$ and $CaCl_2$ deicers. However, it is recognized that NaCl is more corrosive to steel and therefore it is not benign when used as a deicing chemical. Additionally, it is recognized that $MgCl_2$ and $CaCl_2$ are effective at lower temperatures and are commonly used because of this fact. Assuming $MgCl_2$ and $CaCl_2$ will continue to be used, it is even more critical that durable concrete mixture designs be employed by SHAs using these chemicals.

Use of Surface Sealers

Surface sealers effectively reduce or prevent the ingress of moisture, chloride ions, sulfate ions, and other substance that may contribute to damaging reactions in the concrete (Sutter 2008). Concrete surface sealers may be divided into a number of different families, with one such grouping as follows (Cady 1994):

- Water repellants, which penetrate concrete pores to some degree and coat pore walls rendering them hydrophobic (e.g., silanes, siloxanes).
- Pore blockers, which have sufficiently low viscosity to penetrate and seal the pores in concrete while leaving little or no measurable coating on the surface of the concrete (e.g., resins, linseed oil).
- Barrier coatings, which are too viscous to penetrate pores to measurable depths but form surfacing coatings of significant thickness and block the pores (e.g., epoxies, urethanes, and acrylics).

Surface sealers should not be confused with curing compounds, nor should the anticipated use of sealers negate the need for diligent curing efforts (Kosmatka, Kerkhoff, and Panarese 2002). Satisfactory performance of the concrete is still strongly dependent on the development of durable mix designs and effective construction, and surface sealers may be considered in areas where significant deicing chemicals are applied or where concrete durability is suspect. For concrete bridge elements, it is recommended that in order for the use of sealers to be economical, the chloride ion content at the depth of the shallowest 1 percent of the reinforcing steel should be less than 1 lb/yd³ [0.6 kg/m³], and the corrosion potential (half-cell) should be more positive than -250 mV (Cady 1994).

Although all surface sealers can slow the penetration of deicing chemicals, one study showed that siloxane sealants were particularly effective at slowing the ingress of deicing chemicals into concrete or mortar; silane sealants were also effective, but to a lesser extent (Sutter 2008). As a group, silanes and siloxane sealants were the best performers in a Minnesota bridge study, although there was variable performance among products (Hagen 1995).

The application of any surface sealer should be done only on concrete that is clean and allowed to dry for at least 24 hours at temperatures above 60°F [15.6°C]; at least 28 days should be allowed to elapse before applying sealers to new concrete (Kosmatka, Kerkhoff, and Panarese 2002). Application rates and traffic opening times should be in accordance with manufacturers' recommendations. The effectiveness of surface sealers is lost after they are exposed to traffic and environmental forces, and may need to be reapplied after 3 to 5 years (Sutter 2008).

SUMMARY

Deicing chemicals are commonly used as part of winter maintenance activities to provide for safe and efficient travel on the nation's roadways. While effective, these materials also present a potential adverse effect on concrete infrastructure, including pavement, bridges, culverts, and other concrete members.

This document provides guidelines for reducing the effects of chloride salts and other deicers on pavement and structural concrete. The guidelines are presented under different categories of strategies, including 1) durable mix design development, 2) effective construction practices, and 3) post-construction mitigation measures. Table 6 presents an abridged summary of those strategies. Overall, it is most economical to address the long-term durability of concrete structures during the initial mix design and construction processes, but steps can also be taken in the selection and application of deicing materials, and in the protection of the concrete after placement, to effectively balance safety and durability. In the end, the best way to protect concrete from deicer attack is to minimize the exposure and distress potential by using the least amount of deicing chemical possible.

Table 6. Summary of strategies to minimize effects of chemical deicers

Strategy	Recommended Activities
Durable Mix Design	<p>GOAL: Preparation of dense, impermeable mix to resist penetration of deicing chemicals</p> <ul style="list-style-type: none"> • Inclusion of supplementary cementitious materials (SCM) to decrease permeability • Low w/cm (0.45 max) to decrease permeability if protection from corrosion is sought • Durable aggregates not reactive or susceptible to freeze-thaw • Largest nominal maximum coarse aggregate size practical for the project • Consideration of the use of well-graded aggregates • Establishment of adequate air-void system targeted to severity of environmental exposure • Avoid use of chloride-based accelerators • Consideration of water-reducing admixtures and corrosion inhibitors, as appropriate • Assess scaling resistance and electrical conductivity (as a surrogate for permeability) through ASTM C672 and ASTM C1202, respectively.
Effective Construction	<p>GOAL: Construction of well-consolidated concrete free of plastic shrinkage cracks (and other early-age cracking) and without surficial defects</p> <ul style="list-style-type: none"> • Avoid construction under extreme weather conditions • Perform adequate consolidation to remove entrapped air. Ensure internal vibration is effectively applied and vibrating frequency is matched to paving speed. • Use corrosion-resistant dowel bars or tie bars at joints and cracks. • Ensure reinforcing steel has adequate concrete cover (2.5 inches [63.5 mm] suggested). • Ensure bleed water has disappeared before finishing, and avoid overworking surface. • Provide adequate curing using an effective curing compound. Make sure that the proper amount is uniformly applied to the surface. • Employ a 30-day "drying period" before applying deicing chemicals to new concrete.
Post-Construction Mitigation	<p>GOAL: Minimize deleterious effects of deicing chemicals on in-service concrete structures</p> <ul style="list-style-type: none"> • <u>Minimize the application of deicing chemicals and maximize effectiveness of each deicing application.</u> • Use deicing chemicals at lowest possible concentration levels (less than pessimum amount). • Consider increased use of sodium chloride brines wherever possible. • Employ surface sealers (particularly the use of siloxanes or possibly silanes) in areas of heavy deicing applications to reduce ingress of chemicals.

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