

## Tech Brief

# MATERIALS-RELATED DISTRESS: HARDENED CEMENT PASTE

## Best Practices for Jointed Concrete Pavements

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### INTRODUCTION

Concrete is a cemented-aggregate mixture where aggregates are bound together by a cementitious matrix, or hardened cement paste (HCP). Both the aggregates and HCP need to be considered when discussing concrete durability or materials-related distress (MRD).

The purpose of this tech brief is to provide pavement engineers with information to help them specify and choose materials that will last for the desired lifetime of the pavement. This tech brief focuses on considerations for the cementitious matrix with respect to paste-related distress mechanisms. Aggregate-related mechanisms are discussed in a separate parallel tech brief (Taylor and Wang 2015).

### HARDENED CEMENT PASTE

There currently is no definition for hardened cement paste (HCP) within ASTM Committee C09 on Concrete and Concrete Aggregates or the American Concrete Institute (ACI). For the purposes of this tech brief, HCP is considered to include cement, supplementary cementitious materials (SCMs), water, hydration products, any admixtures, and entrained air.

Hardened cement paste forms primarily from the hydration reactions between portland cement and water. Calcium silicate phases in the portland cement hydrate and form the hydration products calcium silicate hydrate (CSH) and calcium hydroxide (CH).

The CSH component provides strength and is desirable. The CH provides little strength and plays a role in most MRD mechanisms because CH is soluble in water and its solubility increases with decreasing temperature. So exposure to water, particularly at low temperatures, results in CH leaching from the concrete thereby increasing the permeability and allowing increased water ingress. In addition, CH is a reactant in some of the deleterious chemical reactions associated with MRDs.

In general, pozzolans (e.g., fly ash, silica fume) are added to concrete mixtures to react with CH and form additional CSH, thereby consuming this undesirable component and decreasing the permeability of concrete. Entrained air is provided to protect the HCP from cyclical freeze-thaw (FT) damage.

Since the discovery of air entrainment, research has been conducted to understand how air voids provide the FT protection observed in practice. Although much has been determined, the exact mechanisms are still not completely understood.

It is known that if an air-void distribution is achieved where the voids are spaced near enough, and the concrete does not become critically saturated (i.e., ~87% of the available pore space filled with water), the paste will be protected from cyclic FT damage (Fagerlund 2004). To achieve the required air void spacing, typically an air content of 2 to 8% by volume of concrete is required (Mindness et al. 2002).



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**Summary of known MRD types due to physical mechanisms**

Type of MRD	Surface Distress Manifestations and Locations	Causes/Mechanisms	Time of Appearance	Prevention or Reduction
Freeze-Thaw Deterioration of Hardened Cement Paste	Scaling, spalling, or map cracking, generally initiating near joints or cracks; possible internal disruption of concrete matrix	Deterioration of saturated cement paste due to repeated freeze-thaw cycles	1–5 years	Add air-entraining agent to establish protective air void system
Deicer Scaling/Deterioration	Scaling or crazing of the slab surface with possible alteration of the concrete pore system and/or the hydrated cement paste leading to staining at joints/cracks	Deicing chemicals can amplify freeze-thaw deterioration and may interact chemically with cement hydration products	1–5 years	Provide minimum cement content of 335 kg/m <sup>3</sup> , limit w/c to no more than 0.45, and provide a minimum 30-day “drying” period after curing before allowing the use of deicers
Freeze-Thaw Deterioration of Aggregate	Cracking parallel to joints and cracks and later spalling; may be accompanied by surface staining	Freezing and thawing of susceptible coarse aggregates results in fracturing and/or excessive dilation of aggregate	10–15 years	Use non-susceptible aggregates or reduce maximum coarse aggregate size

**Summary of known MRD types due to chemical mechanisms**

Type of MRD	Surface Distress Manifestations and Locations	Causes/Mechanisms	Time of Appearance	Prevention or Reduction
Alkali–Silica Reactivity (ASR)	Map cracking over entire slab area and accompanying expansion-related distresses (joint closure, spalling, blowups)	Reaction between alkalis in the pore solution and reactive silica in aggregate resulting in the formation of an expansive gel and degradation of the aggregate particle	5–15 years	Use non-susceptible aggregates, add pozzolans to mix, limit total alkalis in concrete, minimize exposure to moisture, add lithium compounds
Alkali–Carbonate Reactivity (ACR)	Map cracking over entire slab area and accompanying pressure-related distresses (spalling, blowups)	Expansive reaction between alkalis in pore solution and certain carbonate/dolomitic aggregates which commonly involves dedolomitization and brucite formation	5–15 years	Avoid susceptible aggregates, significantly limit total alkalis in concrete, blend susceptible aggregate with quality aggregate or reduce size of reactive aggregate
External Sulfate Attack	Fine cracking near joints and slab edges or map cracking over entire slab area, ultimately resulting in joint or surface deterioration	Expansive formation of ettringite that occurs when external sources of sulfate (e.g., groundwater, deicing chemicals) react with the calcium sulfoaluminates	1–5 years	Use w/c below 0.45, minimize tricalcium aluminate content in cement, use blended cements, use pozzolans
Internal Sulfate Attack	Fine cracking near joints and slab edges or map cracking over entire slab area	Formation of ettringite from internal sources of sulfate that results in either expansive disruption in the paste phase or fills available air voids, reducing freeze-thaw resistance	1–5 years	Minimize internal sources of slowly soluble sulfates, minimize tricalcium aluminate content in cement, avoid high curing temperatures
Corrosion of Embedded Steel	Spalling, cracking, and deterioration at areas above or surrounding embedded steel	Chloride ions penetrate concrete resulting in corrosion of embedded steel, which in turn results in expansion	3–10 years	Reduce concrete permeability, provide adequate concrete cover, protect steel, or use corrosion inhibitor

Tables after Van Dam et al. 2002a

**MATERIALS-RELATED DISTRESS**

Materials-related distress (MRD) refers to “concrete failures that are a direct result of the properties of the material and its interaction with the environment to which it is exposed” (Van Dam et al. 2002a). Failures due to MRD are not related to either inadequate design for the loading conditions encountered or improper construction practices.

Of the MRDs listed in the tables, those affected by the HCP include freeze-thaw deterioration of hardened cement paste, deicer scaling/deterioration, sulfate attack (external and internal), and corrosion of embedded steel. Alkali-aggregate reactivity involves both aggregate and paste and is addressed in the companion tech brief to this one (Taylor and Wang 2015).

**FREEZE-THAW DETERIORATION****What is it?**

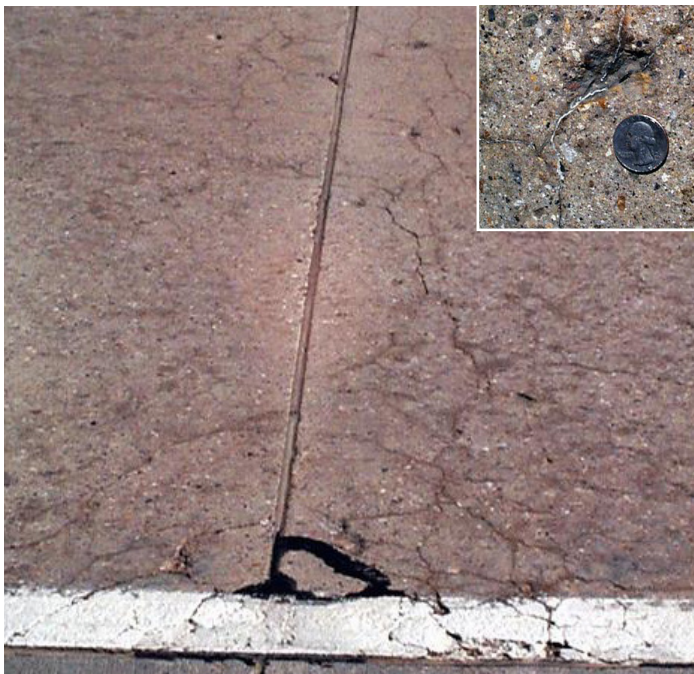
Freeze-thaw (FT) deterioration of HCP, which is generally referred to as FT damage, results when critically saturated HCP undergoes cycles of freezing and thawing. The resulting damage may extend throughout the depth of the concrete section.

Research has shown that when approximately 87% of the pore space in concrete becomes water-filled, even a single FT cycle can result in cracking (Li et al. 2012, Litvan 1988). Entrained air provides additional void space for water to occupy, thereby reducing the degree of saturation. Entrained air also provides void space for ice to form without exerting undue pressure on the surrounding HCP.

There are multiple theories on how water migrates to voids (Powers 1945, Powers 1954, Litvan 1988) but the practical implications are that with an adequate air-void system, HCP is protected from FT damage. More recent research has shown that deicing salts can work to retain water within the pore system even during warmer seasons and that in spite of adequate air entrainment, FT damage can result (Spragg et al. 2011).

**Identification**

Many of the MRD mechanisms affecting HCP, including paste FT, are expansive and manifest as widespread cracking, sometimes with exudate. This type of cracking is referred to as map cracking, as the pattern resembles lines on a road map.



Map cracking commonly seen with freeze-thaw damage and exudate in map crack near the quarter (upper right inset)

In some cases, exudate will be present in the cracks. As discussed in the companion tech brief to this one (Taylor and Wang 2015), other MRDs, such as alkali-silica reactivity (ASR), can have exudate that looks very similar. In the case of paste FT, this exudate is typically calcium carbonate that results from calcium hydroxide (CH) that has leached from the concrete and carbonated in the presence of atmospheric carbon dioxide (CO<sub>2</sub>).

Often, FT can only be inferred as a result of the observed cracking coupled with measurements of the hardened air-void system demonstrating an inadequate air-void system is present. Measurement of the hardened air-void system parameters is done in accordance with ASTM C457 *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete* and is typically performed by a concrete petrographer.

### Prevention

To prevent FT damage, first, it is mandatory to ensure that proper air entrainment is achieved. This requires validation of FT performance at the mixture design stage. Laboratory testing of the mixtures in accordance with ASTM C666 *Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing* is currently the most common means of assessing performance.

Then, as part of construction, proper quality control/quality assurance (QC/QA) measures must be employed to ensure delivery and placement of concrete meeting the established mixture design.

For slip-form paving operations, it is recommended to measure the air content of the fresh concrete before and after the paver because the vibratory process of the paver can affect the air content of some mixtures. Fresh concrete testing for air content is typically performed in accordance with ASTM C231 *Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method*. However, a new air meter has recently been developed and is currently being evaluated by more than 30 state departments of transportation (DOTs).

This new meter, called the Super Air Meter (SAM), provides a fresh concrete measurement that correlates with the spacing factor measurement obtained from ASTM C457 on hardened concrete. Research to date has shown excellent correlation between the SAM meter and ASTM C457, and the American Association of State Highway Transportation Officials (AASHTO) has recently adopted the SAM meter as a provisional test method. The SAM meter offers to provide information about the fresh concrete that to date could only be obtained from analysis of hardened concrete.

Another approach to prevent FT damage is to minimize moisture ingress into the concrete. Penetrating sealers such as silane and siloxane have been demonstrated to drastically reduce water ingress when properly applied (Sutter et al. 2004) but the sealers need to be reapplied every 3 to 5 years. Nonetheless, keeping the water out of the concrete and reducing the degree of saturation can minimize most FT damage.

## DEICER SCALING

### What is it?

Deicer scaling is a form of FT damage that is localized to the surface of the concrete slab. Historically, there has been considerable discussion regarding the mechanism of deicer scaling but recent research indicates the surface layer of HCP delaminates from the remaining slab due to tensile forces in the surface layer of the HCP.

These tensile forces are caused by expansion of the ice layer adhered to the concrete surface (Valenza and Scherer 2007). The expansive forces of the ice are at a maximum when the solution freezing on the surface contains ~3% dissolved salt, and the type of salt is not a factor (Valenza and Scherer 2007).

A well air-entrained HCP resists deicer scaling (Valenza and Scherer 2007) and therefore deicer scaling is often seen where concrete has been over-worked in the finishing step and the air-void system at the concrete surface has been adversely affected.

As the HCP at the surface deteriorates, aggregate becomes freed. Deicer scaling may be progressive, where new layers of HCP are lost with subsequent exposure cycles. However, in many cases, the scaling occurs only in the outermost layer of concrete during a single winter season and then does not progress further in subsequent winter seasons.



*Deicer scaling showing the intact surface on the far left side of the image (left) and close-up of the scaling (right)*

### Identification

Deicer scaling is characterized by a disintegration of the outermost HCP layer on the surface of a concrete slab resulting in a remnant layer of powdered HCP, freed aggregates, or aggregates still in the concrete but clean of cement paste. In some cases, the detrital layer may be transported away by plowing or other activities and only the scaled concrete surface is seen.

As stated, a compromised air-void system at the surface can contribute to scaling but often this is hard to confirm because, as that surface scales off, it is impossible to assess the air-void system that was present. Often cores are obtained from an adjacent intact surface but this concrete may not represent the area that was scaled.

### Prevention

Given that deicer scaling is a form of FT damage, placing concrete that has an adequate air-void system is a requirement for preventing the distress. However, a number of other precautions must also be taken.

Finishing must be performed after the bleed water has risen and dissipated. Finishing the concrete while the bleed process is still occurring can trap water just below the concrete surface, leading to scaling or spalling as the water freezes. Also, finishing the concrete while the bleed water is present will cause that water to be worked into the concrete surface, increasing the water-to-cementitious materials ratio (w/cm) at the surface, creating a weaker HCP that is more susceptible to the physical attack associated with scaling.

Another important precaution when finishing is to not overwork the surface, thereby removing the entrained air from the concrete nearest the surface. This loss of air is a common cause of scaling.

Another general consideration for preventing scaling is proper curing. The curing process must not only prevent moisture loss but also ensure a proper temperature is maintained. Ideally, the concrete would be well cured (e.g., 28 days curing time) and would have had an adequate time to dry prior to freezing (e.g., an additional 28 days of drying after curing). When fly ash or slag cement is used in the concrete mixture, additional time is needed for the concrete to mature (e.g., 56 days curing).

Proper curing leads to strength gain in the concrete and increases its ability to resist the physical forces of FT cycling. Proper curing increases the degree of hydration and thereby reduces the concrete permeability, which improves scaling resistance.

Finally, encourage sparing use of deicers, particularly when the concrete is young (i.e., 1 year or newer). As mentioned, deicer solutions of about 3% salt represent the pessimum concentration at which damage potential is maximized.

After these ordinary steps, penetrating sealers such as silane and siloxane, when properly applied, have been demonstrated to help by reducing water ingress.

## SULFATE ATTACK (EXTERNAL AND INTERNAL)

### What is it?

Sulfate attack is an MRD that is rare in pavements, but has occurred in some cases. Like other chemical attack mechanisms, sulfate attack is complex. It is generally associated with the formation of gypsum through the combination of sulfate and calcium ions, or the formation of ettringite through the combination of sulfate ions and hydrated calcium aluminate (ACI 2008).

The terms internal and external are added to the MRD description to denote the source of sulfate ions. For pavements, external sulfate attack is more common with the sulfate coming from the soil or groundwater. The formation of gypsum can occur by degradation of the HCP and, as a result, the concrete softens and disintegrates.

Ettringite formation as an MRD mechanism in pavements is debated, but it is very common to see ettringite deposits in air voids or cracks of distressed concrete. Although the ettringite formation itself may not cause distress, it is clearly a symptom of water movement through the concrete and every MRD mechanism is exacerbated by water.

Therefore, ettringite formation in air voids and cracks is a general symptom of an environment that could lead to another MRD. Many strongly believe that ettringite infilling of air voids serves to compromise the air-void system and reduce concrete resistance to FT cycles.

### Identification

Deterioration due to external sulfate attack can appear as cracking near joints or the edge of a slab where contact with sulfate-laden water occurs. Fine longitudinal cracking may also occur parallel to longitudinal joints. In advanced cases, the HCP may turn to a non-cohesive powder and the concrete can begin to disintegrate. In other forms, salt crystallization may occur at evaporative fronts and lead to degradation of the concrete at that location.

In the case of ettringite infilling, a petrographer is required to section the concrete sample and examine for infilled voids. It is a matter of professional judgment by the petrographer if the infilled voids compromised the air-void system, resulting in cracking and expansion, or if the concrete cracked from another MRD and the resulting water ingress led to the observed ettringite infilling.

### Prevention

Sulfate attack is minimized first by using a cement low in calcium aluminate ( $C_3A$ ). Examples would be an ASTM C150 (AASHTO M 85) Type II cement or, in the case of high sulfate exposure, a Type V cement. SCMs have also been shown to be effective at mitigating sulfate attack as well as using a w/cm less than 0.45. ACI document ACI 201.2R-08 provides additional guidance on mitigating sulfate attack.

## CORROSION OF EMBEDDED STEEL

### What is it?

Corrosion of embedded steel occurs when the reinforcing steel in the concrete oxidizes (i.e., rusts) resulting initially in staining of the concrete and in advanced cases spalling and cracking as the process advances and a corrosion layer is produced on the outer surface of the embedded steel causing expansion.

Steel embedded in concrete is generally protected from corrosion by the high pH of the concrete pore solution (e.g.,  $pH \approx 13.5$ ). In this high pH environment, a "passivated" layer forms on the steel surface in contact with the concrete and corrosion is inhibited. Chloride ions have the ability to break down this passivated layer and, as that occurs, the corrosion layer is produced. As the volume of the corrosion layer increases near the reinforcing steel, expansive forces are placed on the concrete cover and ultimately cracking and spalling occurs.

The passivated layer can also be compromised by carbonation of the HCP as a result of exposure to atmospheric carbon dioxide ( $CO_2$ ), which can reduce the concrete pH, making the passivated layer unstable. Cracking in the concrete cover facilitates penetration of chloride-bearing fluids as well as  $CO_2$  causing corrosion to be accelerated.



Sutter et al. 2002

*Corrosion of embedded steel where cover layer has spalled*



Sutter et al. 2002

*Hot patch, which subsequently failed from other effects, applied over corrosion of embedded steel where cover layer had spalled*

### Identification

The characteristic rust coloring of exudate from the concrete readily identifies corrosion. This should not be confused with superficial rust stains that may result from abrasion by plows or other means. Ultimately, the concrete cover over the steel will crack and spall, exposing the reinforcing steel.

### Prevention

Corrosion of embedded steel is minimized by first ensuring there is ample concrete cover over the steel. According to the ACI Building Code Requirements for Structural Concrete (2014) and AASHTO Standard Specifications for Highway Bridges (2002), for concrete cast against and permanently exposed to earth, a minimum cover of 3 inches is required.

Penetrating sealers are effective at slowing the ingress of water and chlorides.

## REPAIR

In general, MRDs are difficult to repair given the distresses tend to be progressive and difficult to stop once started. Given that moisture is central to all paste-related MRDs, one general solution for slowing progression of an MRD is to limit moisture exposure. This may be accomplished through sealants, sealers, or other protective measures, or by modifying/retrofitting the drainage surrounding a structure.

In some cases chemical treatments may be available that either halt the reaction or, in some cases, alter the reaction. Testing should be performed with chemical treatments to demonstrate efficacy. Van Dam et al. (2002b) provide an excellent summary of repair and rehabilitation approaches.

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