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DURABILITY OF SAW-CUT JOINTS IN PLAIN CEMENT CONCRETE PAVEMENTS

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16. Abstract

The objective of this project was to evaluate factors influencing the durability of the joints in portland cement concrete pavement in the state of Indiana. Specifically this work evaluated the absorption of water, the absorption of deicing solutions, the relationship between the degree of saturation and concrete deterioration, and the role of Soy Mehyl Esters as a potential concrete sealant. The aforementioned items were studied in conjunction with the observation of premature joint deterioration in concrete pavements. Previous work by the PI identified that deteriorating joints were observed to frequently have standing water and damaged joint sealant. To better understand the potential mechanisms responsible for joint deterioration, a series of mortars were tested that are consistent with the mortar fraction of concrete paving mixtures. The first portion of the work examined the role of deicing salt solutions on the wetting and drying behavior of concrete elements (this was a joint series of experiments with SPR 3093). It was observed that salts altered the equilibrium relative humidity of the solution, as such concrete containing deicing solutions dried less frequently than concrete containing only pore solution. Further, it was observed that the rate of water absorption was related to the square root of ratio of surface tension and viscosity. Salt solutions have a slower rate of absorption than plain water. It was also observed that concrete previously exposed to deicing salts also exhibited an altered rate of water absorption. The second portion of the work examined the concept of the degree of saturation and its relationship with freeze-thaw damage. Specifically mortars with different air contents were examined. Fagerlund developed a model that proposed a critical degree of saturation could be correlated with the onset of freeze-thaw damage. The work suggests that absorption testing should be used to determine the degree of saturation which can be used to estimate the time to reach a critical degree of saturation. Once this critical degree of saturation was reached freeze-thaw damage was inevitable. While entrained air was observed to slow the time to reach a critical degree of saturation, this critical degree of saturation could not be avoided. The final portion of the work examined the potential use of penetrating concrete sealers (like soy methyl esters) to reduce water absorption and the corresponding freeze-thaw damage. While absorption testing was able to show the benefits of sealers, differences were observed regarding the influence of sealer composition on freeze-thaw damage.

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TECHNICAL SUMMARY

DURABILITY OF SAW-CUT JOINTS IN PLAIN CEMENT CONCRETE PAVEMENTS

Introduction

The main objective of this study was to evaluate factors influencing the durability of the joints in portland cement concrete pavement in the state of Indiana.

The scope of the research included the evaluation of the absorption of water in concrete, the absorption of deicing solutions in concrete, the relationship between the degree of saturation and concrete deterioration, and the role of Soy Mehyl Esters (SME) as a potential concrete sealant.

The aforementioned items were studied in conjunction with the observation of premature joint deterioration in concrete pavements. Previous work by the PI identified that deteriorating joints were observed to frequently have standing water and damaged joint sealant. This work was conducted to better understand the potential mechanisms responsible for joint deterioration, a series of mortars were tested that are consistent with the mortar fraction of concrete paving mixtures.

The first portion of the work examined the role of deicing salt solutions on the wetting and drying behavior of concrete elements. The second portion of the work examined the concept of the degree of fluid saturation and its relationship with freeze-thaw damage. The final portion of the work examined the potential use of penetrating concrete sealers (like soy methyl esters) to reduce water absorption and the corresponding freeze-thaw damage.

Findings

The following conclusions can be drawn:

- The rate of fluid absorption (i.e., deicing salt solutions) was related to the square root of ratio of surface tension and viscosity. Salt solutions have a slower rate of absorption than plain water.
- It was also observed that concrete previously exposed to deicing salts also exhibited an altered rate of water absorption. This implies that field concretes can exhibit altered absorption properties depending on previous exposure to salt solutions.
- It was observed that salts altered the equilibrium relative humidity of the solution. As such, concrete containing deicing solutions will not dry (i.e., reduce mass due to water loss) until the humidity is lower than the equilibrium relative humidity of the salt solution. This suggests that concrete in the presence of a salt solution may become preferentially saturated.
- The degree of saturation of the concrete was related to freeze-thaw damage. Specifically, mortars with different air contents were examined. Once this critical degree of saturation was reached freeze-thaw damage was inevitable. Acoustic emission measurements showed that the mortar began to deteriorate for samples where the degree of saturation exceeded 86% saturation. The damage occurred rapidly and took only a few cycles to show substantial degradation.
- The work suggests that absorption testing should be used to determine the degree of saturation which can be used to estimate the time to reach a critical degree of saturation.
- While entrained air was observed to slow the time to reach a critical degree of saturation, this critical degree of saturation could not be avoided.
- Penetrating concrete sealers (like soy methyl esters) reduce water absorption and the corresponding freeze-thaw damage. While absorption testing was able to show the benefits of sealers, differences were observed regarding the influence of sealer composition.

Implementation

The results of this investigation indicate that fluid ingress at the joints in plain jointed cement concrete pavements can lead to deterioration caused by freezing and thawing.

It is believed that the joints will contain a high salt concentration as the deicing solutions are held at the joints if they cannot drain. The results demonstrate that salt in the solution can alter the viscosity and can slow the rate of saturation. Despite a slower ingress, deicing solutions can also alter the drying rate limiting or preventing the amount of drying that can occur at the concrete joints.

Absorption tests on mortar without air entrainment reached a critical degree of saturation after only 4 to 5 months; however air entrained systems reached a critical degree of saturation after approximately 6 years. Soy Methyl Ester – Polystyrene blends (SME-PS) alter the rate of fluid absorption and reduce the potential for freeze-thaw damage.

It is recommended that the design of longitudinal and transverse joints in portland cement concrete pavements in Indiana be reconsidered. When considering only the durability of the concrete joint it appears that removing the conventional sealant and sealing the concrete with a penetrating sealer may extend the life of the joint. The redesign of the joint however also considers the potential for incompressible materials to enter the joint. Further the redesign of the joint requires that the subgrade is able to function properly with additional fluid that may come through the joint.

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CHAPTER 1: INTRODUCTION

1.1 Background

The D-1 and longitudinal joints in concrete pavements are a constant source of maintenance problems for the INDOT. Further, these joints have demonstrated in some cases, the propensity to exhibit premature deterioration which can necessitate repair. As such, an examination of issues surrounding the performance of these construction joints is warranted.

Current INDOT specifications require that the contractor place an initial saw-cut in the concrete pavement shortly after the pavement is placed. This initial saw-cut is used to control random cracking. A previous INDOT study examined the time that this saw-cut should be placed (1). In that study computer simulations were performed to indicate how the time of saw-cutting varied depending on the mixture proportions, the saw-cut geometry, and the environmental conditions. The previous study provided substantial insight into the time that the saw-cuts should be placed as well as how this timing need to be altered due to changes in mixture proportioning, environmental conditions, and saw-cut geometry. It should be noted however that several questions were raised that were beyond the scope of the earlier study. These questions revolved around the durability of the joints, especially in light of premature joint deterioration that has been observed in several pavements.

This project was designed to provide information on the potential for water (or fluid containing deicing salt solutions) penetration leading to joint deterioration. Additionally, the potential use of a concrete sealer was evaluated as a method to reduce fluid penetration

1.2 Research Objective and Organization of the Report

The objective of this project is three-fold.

- First, the project will evaluate the similarities and differences between drying and wetting of water and solutions containing deicing salts. This work is outlined in chapter 2.
- Second, the project will evaluate the role of the degree of saturation in determining the freeze-thaw behavior of concrete. It is proposed that concrete will exhibit freeze-thaw deterioration once a critical degree of saturation is reached. Chapter 3 describes the role of air entrainment in altering the degree of saturation and extending the time that it takes for freeze-thaw damage to occur.
- Third, the project will evaluate the potential role of concrete sealers in reducing fluid transport at or near saw-cuts in pavements. Chapter 4 describes the potential role that concrete sealers can play in extending the life of concrete pavement joints.

Chapter 5 will provide short summary of the salient results obtained from this study. More importantly it will provide recommendations to INDOT for consideration in joint design and maintenance. This will also provide suggestions for items to consider in future studies. The information from this report is one step forward in improving the quality of concrete pavements and most importantly the durability of the joints in the concrete pavements.

CHAPTER 2: WETTING AND DRYING OF CONCRETE IN THE PRESENCE OF DEICING SALT SOLUTIONS

2.1 Overview

A series of wetting and drying tests were performed on concrete using different aqueous solutions containing deicing salts. The rate of absorption was generally lower for aqueous solutions containing deicing salts. In addition, less fluid was absorbed for aqueous solutions containing deicing salts. The change in the rate of aqueous fluid absorption was proportional to the square root of the ratio of surface tension and viscosity of the absorbed fluid. Concrete that has been exposed to solutions containing deicer salts show less mass loss during drying. Measures of equilibrium relative humidity over the salt solutions are used to interpret drying behavior. Experimental data indicates that concretes that have previously been exposed to deicing solutions can also exhibit reduced rate of absorption, even if water is used as the fluid being absorbed.

2.2 Introduction

Some jointed plain portland cement concrete pavements in freezing prone climates have shown premature deterioration at the longitudinal and transverse joints. While some have attributed this damage to a chemical attack, inadequate air entrainment, poor mixture design, inadequate constituent materials, or poor construction practices; it is the hypothesis of the authors of this paper that this joint deterioration may be attributed, at least in part, to preferential absorption of fluid at joints. This hypothesis was developed based on observations from the field that show these deteriorated locations frequently occurred at low spots in the pavement, where joint sealers were damaged, where water has collected, or where the joint does not appear to have opened thereby trapping water (2). Preferential fluid ingress at joints could increase a variety of damage mechanisms including deleterious chemical reactions, crystallization pressure, or freeze-thaw damage that may degrade the concrete. To fully evaluate fluid ingress at the joints it is essential that the wetting and drying behavior of concrete is evaluated using aqueous solutions containing deicing salts. It should be noted that some members of the SAC have pointed out that some similar distresses have been observed at other locations in concrete pavements and it has been stated that some of these locations may or may not have standing water and preferential ingress. This report is not intended to address those locations; rather, it addresses behavior in the joints focusing on the role of water absorption.

This work is limited in scope as it considers only the ingress of aqueous solutions over short time periods

and does not explicitly consider any chemical reaction that occurs between the aqueous solution and the concrete or any long-term effects. This information is intended to provide reference for those developing tests to evaluate potential deicer-concrete interactions (3), for developing tests on fluid absorption, for evaluating fluid absorption in concrete (4), for input parameters in computer simulation of fluid ingress at joints (5), and for potential approaches to limit joint deterioration like penetrating sealers for possible use in concrete pavements (6).

2.3 Fluid Absorption in Porous Materials

Fluid absorption is a frequently used test to provide an indication of the durability of concrete systems since it is simple to perform. Several standard tests exist for measuring water absorption including ASTM C 1585-04 (7), BS 1881-99 (8), and ASTM D6489-99 (9). While the concept behind these tests is very similar, there are differences in how the samples are conditioned, treated, and tested. In each of these tests water is typically used as the fluid that is being absorbed. Hall (10) discusses that water can interact with the cement matrix adding complexity to the interpretation of results. To overcome some of these limitations or to indicate how absorption can be reduced by fluid composition other solutions have been tested (10,11,12,13,14).

MacInnis and Nathawad (15) assessed the absorption of an aqueous solution consisting of a NaCl deicing salt and reported a decrease in absorption. Sutter et al. (16) reported that sorptivity decreased from highest to lowest in the order of water, NaCl, $CaCl_2$ and $MgCl_2$. Similar data has recently been observed by Janusz (17). As a result, it can be observed that concrete exposed to deicing salt solutions absorb fluid at a slower rate than they would absorb water; however the previous work has not related this behavior to the fluid properties or described the influence of salt concentration or properties of the aqueous solution.

The results of one-dimensional fluid absorption tests (assuming negligible gravitational effects) are typically reported as the cumulative water absorbed per surface area (surface from which water is absorbed) versus the square root of wetting time. Equation 2.1 can be used to describe the water absorption (total volume of fluid absorbed) and the sorptivity (related to the rate of absorption).

$$i = S\tau^{1/2} \tag{2.1}$$

where i [mm^3/mm^2] is the cumulative water absorption, S [$mm/s^{1/2}$] is the sorptivity, and τ [s] is the elapsed time.

Hall (10) proposed that the diffusion would scale proportionately with the ratio of surface tension (γ) and viscosity (η) of the fluid. Hall further related this to sorptivity since sorptivity is related to the square root of diffusion. Kelham (18) derived an expression for fluid absorption (Equation 2.2) that shows the relationship between depth of penetration and the square root of the ratio of surface tension and viscosity.

$$x(\tau) = \sqrt{\frac{4k\gamma\cos(\theta)\tau}{p\eta r}} \tag{2.2}$$

where $x(\tau)$ [mm] is the penetration depth, γ [N/mm] is the surface tension, θ [rad] is the liquid-solid contact angle, p [~] is the porosity of the medium, r [mm] is the pore radius, k [mm^2] is the intrinsic permeability of the material, and η [Pa.s] is the viscosity of fluid. An expression similar to equation 2.2 was derived by Scherer and Wheeler (19) for stone consolidates.

Previous research using organic fluids have been noticed to have an absorption rate that scales proportionally with the square root of the ratio of surface tension and viscosity of the fluid ($(\gamma/\eta)^{1/2}$). This work will use this approach to attempt to interpret results from absorption tests that used aqueous solutions containing deicing salts.

2.4 Wetting and Drying for Concrete with Deicing Solutions

2.4.1 Experimental Program of Wetting and Drying of Concrete with Deicing Solutions

The concrete mixture that was used for these tests was a typical INDOT class C bridge deck concrete. A bridge deck concrete was selected since it was available from a previous study and had been conditioned for a long period of time. It is believed that from a fluid absorption perspective there is little difference in the fundamental mechanisms of absorption between the concretes. These concretes will however have different paste/aggregate volumes. The mixture proportions of this concrete are shown in Table 2.1. The fresh air content was 5.7% measured according to ASTM C231-09 (20). The hardened air content of the concrete was 4.4% as assessed using an automated optical scanning approach (21) based on the approach of Peterson et al. (22).

The concrete was produced in a central mix plant and discharged from a ready mix concrete truck before the concrete was sampled. A series of 100 mm × 200 mm cylinders were cast. After one day of curing, the cylinders

TABLE 2.1
Mixture Proportions Assuming Saturated Surface Dry (SSD) Conditions

Material	Mass
Cement (kg/m^3)	316
Class C Fly Ash (kg/m3)	60
Water (kg/m^3)	150
Fine Aggregate (kg/m^3)	736
Coarse Aggregate (kg/m^3)	1049
Air Entrained Admix. (ml/ 100 kg cem. materials)	20
High Range Water Reducer Admix. (ml/ 100 kg cem. materials)	456
Retarder Admixture (ml/ 100 kg cem. materials)	98

were demolded and sealed in double plastic bags at 23 ± 0.5 ℃ until the samples reached an age of 28 d. After 28 days of curing the cylinders were removed from bags and three 50 mm ± 2 mm thick samples were cut from the central portion of each cylinder with a wet saw.

Two different series were used to condition the concrete samples. The first series evaluated the role of different conditioning regimes on the absorption of water using three samples for each curing condition. The samples in the first series were conditioned in five different ways (ASTM, oven-dry, 50% relative humidity (RH), 65% RH and 80% RH). A portion of the samples were conditioned following the procedure in ASTM C1585-04 (after conditioning the samples for 12 months at 50% RH they were vacuum saturated for 24 h and then exposed to ASTM C1585-04 conditions). The remaining samples were conditioned in four different ways: 1) at 80% RH for 12 months, 2) at 65% for 12 months, 3) at 50% for 12 months, and 4) oven dried. The second series of samples consists of concrete samples that were dried at 50 ± 2% RH, 23 ± 0.5 ℃ for 36 months and two samples were tested for each curing condition.

To prepare the specimens for fluid absorption testing the sides of the sample were sealed with epoxy. After the epoxy had hardened the top surface was covered with plastic to avoid evaporation from the sample during testing.

The absorption test involves recording incremental mass change measurements during the first six hours after the sample comes in contact with the fluid and subsequently taking one measurement every day for the next eight days. The amount of absorbed fluid is normalized by the cross-section area of the specimen exposed to the fluid using Equation 2.3.

$$i = \frac{m_t}{(a \cdot \rho)} \qquad (2.3)$$

where: i (mm^3/mm^2) is the normalized absorbed fluid, m_t (g) is the change in specimen mass at time t; a (mm^2) is the area of the specimen exposed to the fluid (i.e., that of the bottom face), and ρ (g/mm^3) is the density of the absorbed fluid (this is provided in greater detail later in the paper). These absorption measurements are then plotted as a function of the square root of time. The sorptivity is the slope of this graph.

The second series of samples were tested using seven different fluids. Their composition primarily based upon, one of three different industrially available deicing products, either NaCl, $MgCl_2$ or $CaCl_2$. A low concentration was used for each salt as well as a higher concentration that was selected to be near the eutectic composition for each salt. De-ionized water was also used as a reference fluid.

2.4.2 Experimental Results from Wetting with Different Conditioning Methods

Figure 2.1 shows the results from water absorption tests performed on the first series of samples that were conditioned with different environmental conditions as

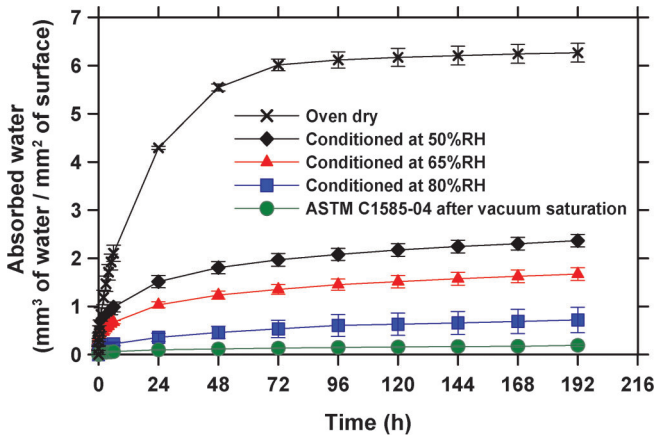

Figure 2.1 Water Absorption on Samples Subjected to Different Conditioning Procedures

mentioned earlier (ASTM C1585-04 accelerated conditioning, 80% RH, 65% RH, 50% RH and oven drying). It should be remembered that these samples were conditioned for 12 months while the remainder of the samples discussed in this paper were conditioned at 50% RH for a much longer time. Sample preparation has an enormous impact on the water absorption results as more severe drying enables a greater volume of water to be absorbed during the test.

2.4.3 Experimental Results from Wetting and Drying with Deicing Solutions

Figure 2.2 illustrates the results of the fluid absorption test as a function of time (for concrete at 50% RH for a longer conditioning time than the samples in Figure 2.1). It can be seen that even though the concrete that is used for all the tests in Figure 2.2 has the same conditioning and exposure conditions, the volume of solution absorbed by each material is dependent on the deicing salt solution and the concentration of the deicing salt solution that was

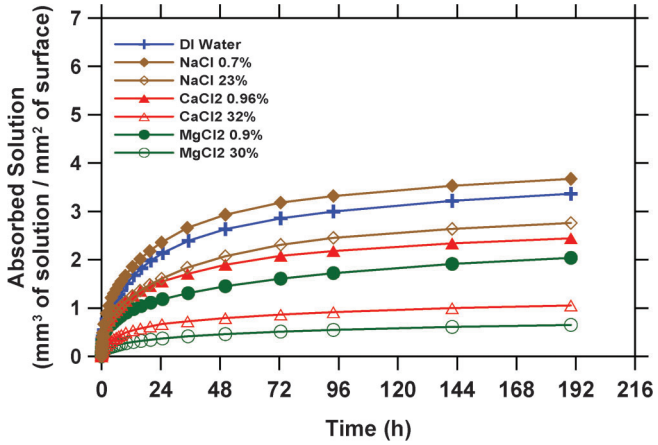

Figure 2.2 Volume of Deicing Solutions Absorbed by Concrete as a Function of Time (Typical Standard Deviation less than 0.1 mm^3/mm^2)

absorbed. The sample with the low concentration of NaCl showed a slight increase in the rate of absorption (as compared with water) as well as the amount of fluid absorbed. This is consistent with the data reported by MacInnis and Nathawad (15). The absorption of all the other fluids was reduced when compared with water. As a result it can be concluded that in general as the salt concentration increased a reduced rate of absorption and reduced total absorption was observed. Further work is needed to examine lower concentrations for NaCl to ascertain why a slight increase is typically reported.

After the fluid absorption test was performed for 8 days the samples were dried at 50 ± 2% RH, 23 ± 0.5 ℃ for seven days. The samples were kept in the same one-faced exposed condition for the drying test; however, the exposed surface that was facing down in the absorption testing was placed facing up to simulate drying from the top. During the drying test the mass of the samples was recorded at regular intervals.

Figure 2.3 shows the volume of water loss during the drying period. It is important to note that the drying test will result in only the water portion of the solution being evaporated from the system leaving the salt to become more concentrated in the solution before it eventually precipitates out. It can be noticed that as the concentration of deicing solution was increased the mass loss during drying decreased. This was particularly evident in the high concentration solutions which showed nearly no mass loss or even a slight gain during drying.

2.4.4 Experimental Results from Wetting Previously Exposed to Deicing Solutions

The samples that were first tested for absorption of different aqueous solutions, then tested for drying, were then oven dried so that a second fluid absorption test could be performed. The second fluid absorption test however used only de-ionized water as the fluid that was being absorbed.

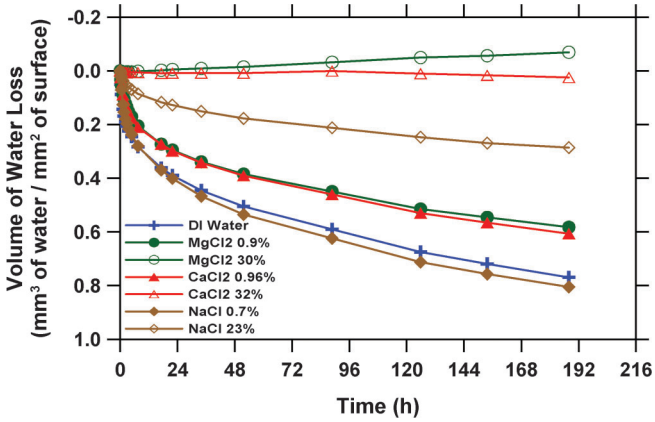

Figure 2.3 Drying of Concrete Prewetted with Different Salt Solutions as a Function of Time (Typical Standard Deviation less than 0.03 mm^3 water/mm^2)

To prepare the samples for the second wetting test they were placed in an oven at 105 ± 2 ℃ until the difference between any two 24 h apart successive mass measurements were less than 0.5% (i.e., approximately 5 days). It is important to note that this drying process will evaporate only the water portion of the solution pre-absorbed, leaving salt in the pores. Since these samples were oven dried, their absorption rates and absorbed water are not comparable with any previous tests.

Figure 2.4 shows the results for this second absorption test. It can be seen by comparing the results to the results in Figure 2.2 that the behavior of the samples was dependent on the deicing solutions and the concentrations of deicing solutions used in the first wetting test. These results are a clear indication that the history of the samples affects the results of fluid absorption. This suggests when sorption testing is preformed on field concretes some understanding of the admixtures or salts that remain in the pore system is needed to fully interpret the results.

2.4.5 Drying of Mortars Saturated with Different Deicing Salts

Moisture desorption is an established technique for evaluating the effect of moisture loss at a given humidity for a material. A TA Q5000 SA moisture sorption analyzer was used to carefully control temperature and humidity. Mortar samples were prepared (w/c = 0.42 and 55% aggregate by volume) and cast in a cylindrical mold with a 34 mm diameter and 50 mm height. At an age of 28 days the specimens were demolded and 34 mm diameter 0.8 ± 0.05 mm thick slices were taken from the middle of the samples. The samples were dried under controlled conditions (at 23 ± 0.1 ℃ and 50 ± 1% RH) in a CO_2 free chamber until they reach mass equilibrium. Then, samples were submerged for a minimum of 5 days in aqueous

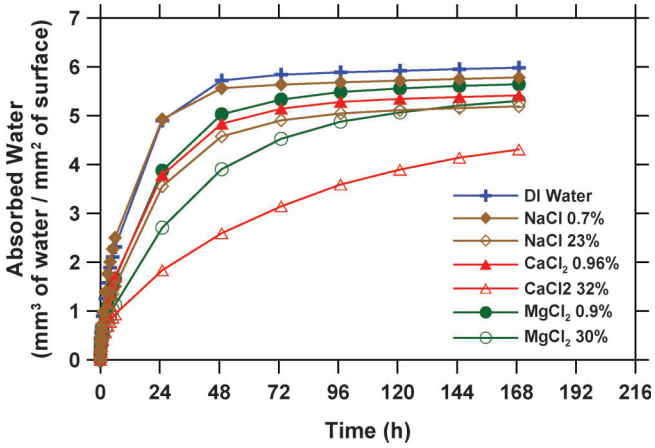

Figure 2.4 Volume of De-ionized Water Absorbed by Concrete as a Function of Time in the Second Fluid Absorption Test (Fluid from the Original Test is Shown in the Caption)

solutions with 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$ by mass.

For the samples submerged in NaCl, $CaCl_2$, and $MgCl_2$ solution,s a 50 mg to 70 mg piece of sample was placed in a tared quartz pan after a minimum of 5 days of submersion. The pan containing the sample was then suspended from the balance ($\pm$ 0.001 mg accuracy) and placed in the relative humidity chamber to equilibrate at 23.0 $\pm$ 0.1 ℃ and 97.5 $\pm$ 0.1% RH for up to 96 h or until the sample had achieved a stable mass (less than an 0.001% mass change/15 minutes).

Then, the relative humidity was reduced to reach 95%. After the sample mass equilibrated, the relative humidity in the chamber was changed in 10% RH steps to 55% RH, allowing the sample to attempt to equilibrate (12 h or 0.01% change in mass over 15 minutes) at each new humidity. After equilibrating at 55% RH the samples were dried to 0% RH. For the sample submerged in de-ionized water the procedure was similar, but the relative humidity was reduced in 5% steps from 97.5% to 2.5%, and then reduced to 0% RH.

Figure 2.5 shows the plot of mass change as a function of time for the mortar saturated in de-ionized water. The sample soaked in water can be seen to lose mass with the decrease of RH. For this system, when the environment is below 100% RH, water will move from the pores to outside of the sample and classical drying behavior is observed. The maximum mass of the sample is 8.5% higher than the mass of the oven dry sample.

Figure 2.6 shows a plot of mass change for the mortar samples submerged in aqueous solutions of 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$. It can be observed that initially upon placement in the testing chamber at 97.5% relative humidity the mass of the sample increases for the first 96 h until the relative humidity of the chamber is changed. The samples absorb water during this time of preconditioning, with values much higher than the 8.5% increase in mass of the sample with de-ionized water as compared with the oven dry sample.

The sample loses weight as the relative humidity is decreased however it should be noted that the sample mass does not decrease to below the initial mass obtained from soaking the sample in the deicing solution until relative humidity was decreased below 85%, 55% and 55% for NaCl, $CaCl_2$ and $MgCl_2$ respectively. This will be compared with the equilibrium relative humidity of the salt solution later in the paper.

2.5 Properties of Deicing Salt Solutions

Physical properties of pure solutions were gathered from literature and compared with measured values for the industrially available deicing solutions tested in this research, and they are provided here for convenience in one location. The properties of the deicing solutions will be used in interpreting the wetting and drying results. This section is divided into four sections. The first three sections describe the influence of the deicing solutions in terms of surface tension, viscosity, and equilibrium relative humidity over the aqueous solution. The fourth section describes the specific gravity of the solution as a function of concentration as this is used to determine the volume of solution absorbed during the absorption test.

2.5.1 Surface Tension of Deicing Salt Solutions

Figure 2.7a shows surface tension measurements at different concentrations for the three solutions used in this research: NaCl, $CaCl_2$, $MgCl_2$. The surface tension for NaCl was obtained from (11), $CaCl_2$ from (23) and $MgCl_2$ from (24). A Du Noüy Ring Tensiometer KRÜSS was used with a resolution of 0.1 mN/m for the industrial deicers tested in this study. The tensiometer was cleaned between measurements following ASTM D971-04 (25). The tensiometer was first calibrated using de-ionized water, which provided a value of 71.0 $\times$ 10^{-6} N/mm. A series of three measurements were performed for each solution, with the average reported.

The closed points in Figure 2.7a are the values measured for the industrially available solutions. The

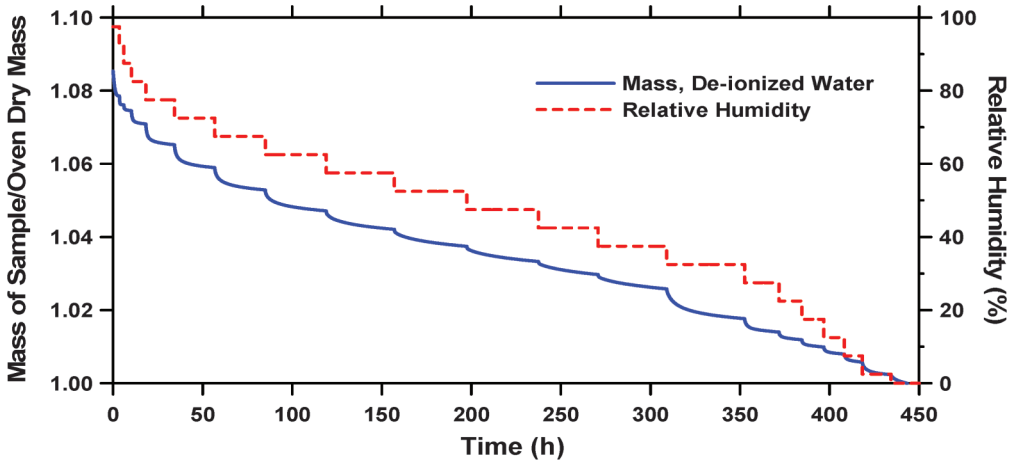

Figure 2.5 Mass Change at Decreasing RH for Samples Containing De-ionized Water

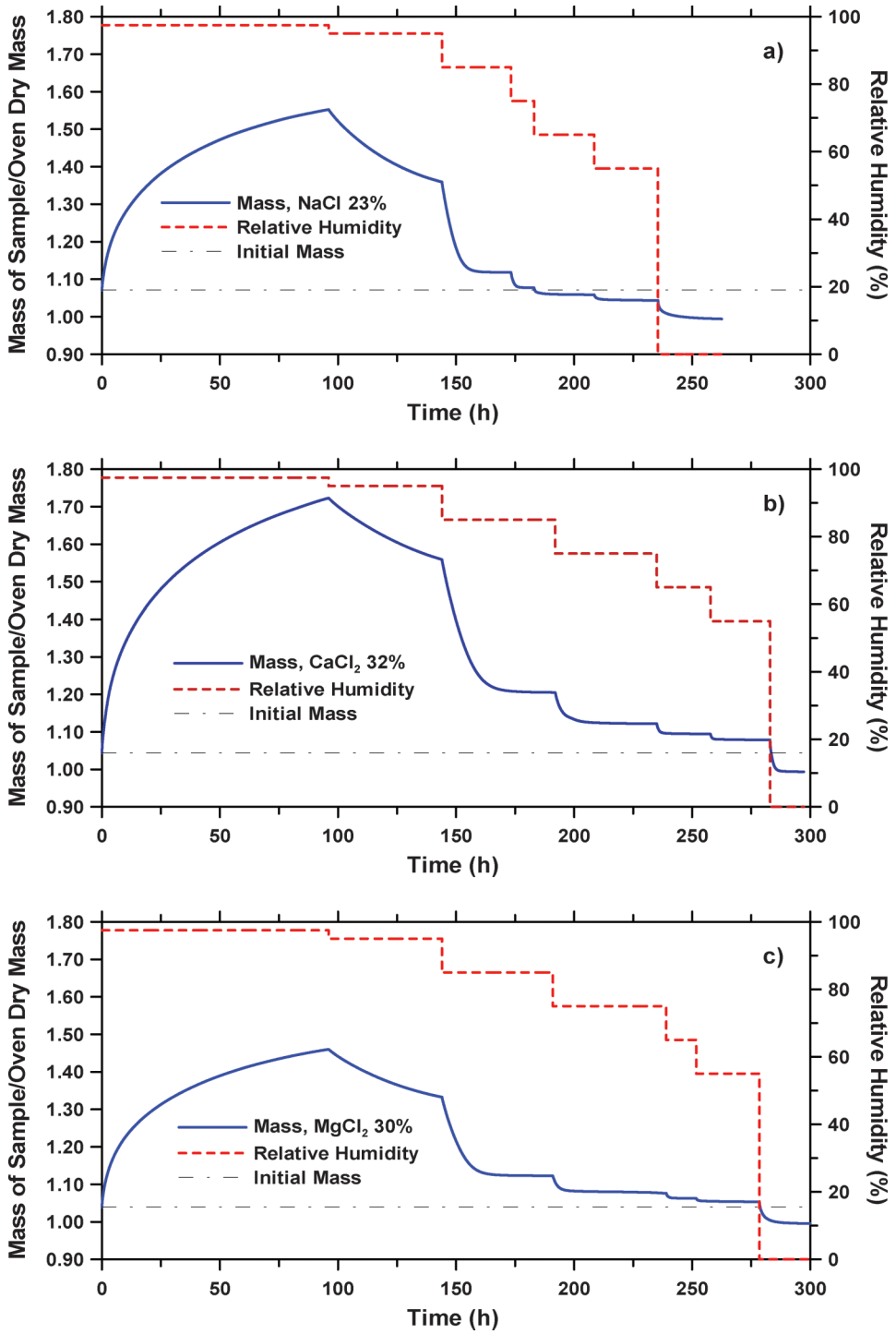

Figure 2.6 Mass Change for Samples Submerged in Aqueous Solutions Containing Deicing Salts: (a) NaCl 23% (b) $CaCl_2$ 32% and (c) $MgCl_2$ 30%

lines represent values taken from literature for pure salt solutions at different mass concentrations. While the general trends are consistent, differences between the solutions containing industrial deicing salts and literature values may be due to impurities or other additives however further work is needed to examine this in greater detail.

2.5.2 Viscosity of Deicing Salt Solutions

Figure 2.7b shows a comparison of the viscosities for the solutions used in this research between pure solutions taken from literature and measurements of the deicing solutions. Viscosity measurements for the industrial deicers were performed on the salt solutions using an

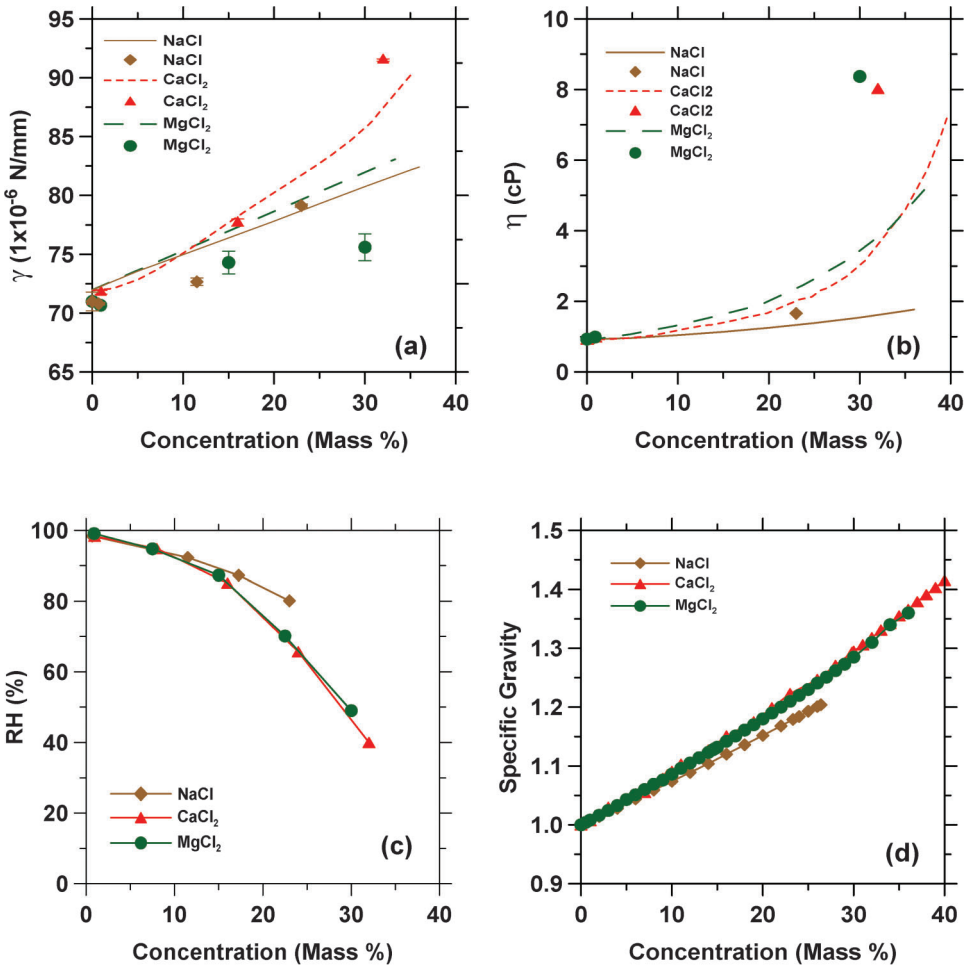

Figure 2.7 Properties of Deicing Salts at 23–25 ℃: (a) Surface Tension (b) Viscosity (c) Relative Humidity (d) Specific Gravity (27)

Anton-Parr rheometer, model Physica MCR 301. The rheometer kept the solution being tested at 23.0 ± 0.02 ℃ and from the torque applied to the fluid that causes a shear from which the viscosity can be found. Calibration of the device was performed using a reference standard.

The dashed lines presented are viscosities at different concentrations and are taken from literature (11,23,24,26), while the points represent measured viscosities of the industrially available solutions. Again, differences between literature values and those of the solutions measured can be explained by differences in possible additions or chemistries of the industrial deicers.

2.5.3 Relative Humidity of Deicing Salt Solutions

Relative humidity measurements were performed on the salt solutions using Rotronic HygrClip2S sensors (± 0.8% RH at 23 ± 0.1 ℃). The relative humidity probes were mounted in a 75 mm × 68 mm stainless steel cylinder that was placed over a water jacketed sample cup holder. The water jacket was connected with a water bath at a constant temperature of 23.0 ± 0.1 ℃.

Figure 2.7c shows the relative humidity measured over salt solutions for a wide range of solution concentrations. As the concentration increased the relative humidity over the solution decreased. The measured relative humidities of these unsaturated salt solutions are higher than that of the saturated solution of these salts which are 75.4% RH for NaCl (28), 33.0% RH for $MgCl_2$ (28) and 22% for $CaCl_2$ (23).

2.5.4 Specific Gravity of Deicing Salt Solutions

Figure 2.7d shows the specific gravity of different deicing solutions as a function of concentration. The specific gravity of the solution increases with concentration. The $CaCl_2$ and $MgCl_2$ increase at very similar rates with an increase in concentration, while the NaCl increases slightly less than the $CaCl_2$ and $MgCl_2$ (i.e., 25% less increase with concentration). This may be attributed to the colligative properties of solutions (29).

2.6 Discussion of Results

2.6.1 Aqueous Solution Absorption Behavior as a Function of Surface Tension and Viscosity

Equation 2.3 showed that the rate of absorption was related to the square root of surface tension and

viscosity. Figure 2.8 plots the square root of the ratio of surface tension and viscosity versus mass concentration of salt. Pure salt solutions are shown as lines while industrial deicing solutions are presented as solid points, and the open points represent the measured sorption response of concrete (i.e., salt sorptivity/water sorptivity) from Figure 2.2. Figure 2.8 confirms that as the solution concentration increases, the rate of fluid absorption (i.e., sorptivity) decreases. Further, while the properties of pure solutions may not exactly represent the response of industrially available deicing solutions they do provide a comparable trend. Reasonable agreement is seen between the measured sorption and square root of the ratio of surface tension and viscosity the measured properties. Additional work is currently being performed to extend these results to a wide range of temperatures.

2.6.2 Drying Time Versus Wetting Time

Comparing Figure 2.2 and 2.3 indicates that wetting happens much faster than drying. When de-ionized water was used as the absorbed fluid, the amount of fluid that was evaporated from the sample after eight days was 0.8 mm^3/mm^2. In contrast, it took just two hours for samples to absorb the same amount of fluid. These differences are even larger when salt solutions were used as the absorbed fluid. When $MgCl_2$ solution was used as the absorbed fluid, the amount of fluid that was evaporated from the sample after eight days was 0.07 mm^3/mm^2, but it took just ten minutes for the samples to absorb the same amount of fluid.

This is important as it suggests that field concrete may be more susceptible to increasing its level of saturation over time rather than drying out. Further, it shows that laboratory tests that use equal times for drying and wetting increase the saturation level of the concrete over time. Researchers (30) observed an increase in sample mass during wetting and drying cycling with deicers which was attributed to microcracking; however an increase in mass would be consistent with the wetting and behavior observed in this paper.

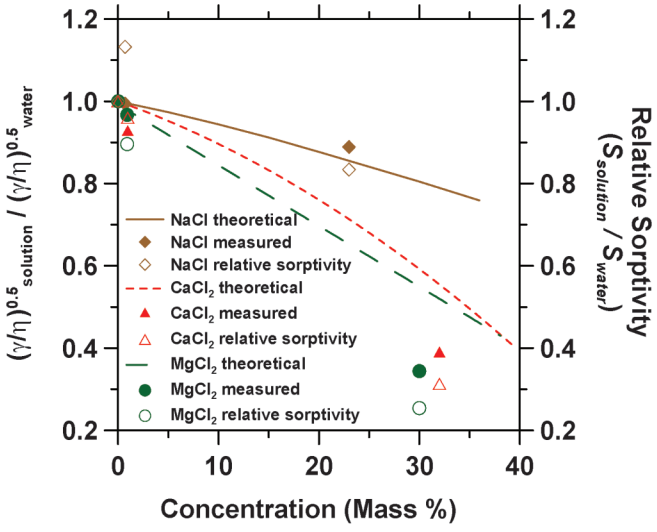

Figure 2.8 Relative Sorptivity for Deicing Solutions

2.6.3 Reduced Drying with Salt Solutions – The Role of Solution Equilibrium Humidity

The relative humidity of different salt solutions presented in Figure 2.7b help to understand the results from the drying tests. The equilibrium relative humidity for the 23% NaCl, 32% $CaCl_2$ and 30% $MgCl_2$ solutions are 80%, 40% and 50% respectively. When the samples are placed in an environment with a relative humidity that is greater than or equivalent to the approximate equilibrium relative humidity over the aqueous solution in the pores water will not be lost (Figure 2.3) and the sample can actually gain mass (Figure 2.3 and 2.6). This can be seen by the thinner (dashed lines in Figure 2.6), which show the initial mass of the sample after it has been submerged in a aqueous solution for over 5 days. At relative humidity higher than the equilibrium of the aqueous salt solution the samples will increase in mass. At relative humidities where the environment is less than the equilibrium humidity over the salt solution, the samples will be expected to decrease in mass. The drying behavior of systems containing concentrated aqueous solutions of deicing salts is complex and requires additional research.

2.6.4 Effect of Solution on Rewetting

When samples of concrete that were previously exposed to deicing solutions were rewet with water they had an absorption and rate of absorption that depended on the history of the specimens (Figure 2.4). The absorption of water can be 30% to 50% less in specimens that were exposed to deicing solutions at some point in their lives. This is an important, yet subtle, factor to understand. This is important since absorption tests of field concrete may be mistakenly interpreted by relating the reduction in sorption to pore filling or delayed sorption microcracking. Both of these observations (lower sorptivity and delayed sorption) are consistent with data here for samples that did not have reduced porosity or differences in sample damage.

2.7 Summary and Conclusions

This paper has reported experimental results from aqueous solution absorption measurements and drying measurements for concrete in the presence of deicing solutions. The following observations can be made. First, the absorption of fluid in concrete depends on the drying environment used to condition the samples. Samples stored at a lower RH absorbed a greater volume of fluid. Second, it was observed that the deicing solutions reduce the rate of fluid absorption. This reduction can be related to the square root of the ratio of surface tension and viscosity (11). Third, the time scale between drying and wetting is different and

concrete is more likely to become preferentially increasingly wet over time. Fourth, the drying of concrete containing aqueous solutions (with deicers) differs from that of water. The equilibrium relative humidity of the aqueous solution plays an important role on limiting drying. Finally, the presence of deicing salts in field samples impacts the absorption when field samples are tested in the lab using water. This suggests that care must be taken in analyzing field concrete exposed to deicing salt solutions.

CHAPTER 3: WATER ABSORPTION AND CRITICAL DEGREE OF SATURATION AS IT RELATES TO FREEZE-THAW DAMAGE IN CONCRETE PAVEMENT JOINTS

Fluid ingress is a primary factor that influences freeze-thaw damage in concrete. This paper discusses the influence of fluid ingress on freeze-thaw damage development. Specifically, this paper examines the influence of entrained air content on the rate of water absorption, the degree of saturation, and the relationship between the saturation level and freeze-thaw damage. The results indicate that while air content delays the time it takes for concrete to reach a critical degree of saturation it will not prevent the freeze-thaw damage from occurring. The results of the experiments show that when the degree of saturation exceeds 86 to 88% freeze-thaw damage is inevitable with or without entrained air, even with very few freeze-thaw cycles.

3.1 Background on the Problem of Joint Deterioration in Concrete Pavements

Concrete pavements represent a large portion of the transportation infrastructure. While many of these pavements provide excellent long-term performance, a portion of these pavements have recently shown premature joint deterioration throughout the Midwestern states (31,32,33,34). This joint deterioration is problematic since it compromises the performance and potential service life of an otherwise healthy pavement. Figure 3.1 shows photographs of a typical damaged pavement joint. This type of damage is frequently seen as either the development of cracking parallel to the joint or spalling and cracking at the joint from the bottom of the saw cut to the surface of pavement approximately 4 to 6 inches from the joint. Unfortunately damage is not frequently observed at the surface of the pavement until a significant amount of damage has occurred inside the joint. During field inspections it has been observed that where the joints are damaged the sealant is damaged and the joint contained standing water. Research is needed to better understand how this standing water may lead to freeze-thaw damage. Further, this damage occurs in both poorly air entrained and properly air entrained concrete. As a result the role of air content needed to be quantified which is the reason for this study.

3.2 Background on Water Absorption and the Critical Degree of Saturation

Concrete is susceptible to freeze and thaw damage when it is saturated (32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49).

While the water content in concrete can be quantified in several different ways, this paper defines the degree of saturation (S) as the ratio of the absolute volume of absorbed water to the total volume of pores (i.e., the total volume of water that can be absorbed by concrete).

It has been suggested that there is a critical degree of saturation (S_{cr}) beyond which freeze and thaw damage can begin to initiate. For degrees of saturation below the critical degree of saturation freeze-thaw damage is not observed to occur even after a large number of freeze-thaw cycles (35,36,37,38,40,41,42,43,44).

Figure 3.2 schematically illustrates the concept of water absorption and the critical degree of saturation (40,51). We can begin by assuming that the representative volume element shown in Figure 3.2 is filled with pores with different sizes at a given spacing. It is assumed that there are two critical values that describe the freeze-thaw performance. The first parameter is related to the degree of saturation as described above. The second parameter is related to a "critical flow distance" (i.e., D_{cr}), which is the maximum distance that water can flow from freezing site to the surrounding nearest air-filled space. Damage doesn't occur when the flow distance (D) is below the critical distance (D_{cr}) and the degree of

Figure 3.1 Photograph of field observation showing damage in pavement joints

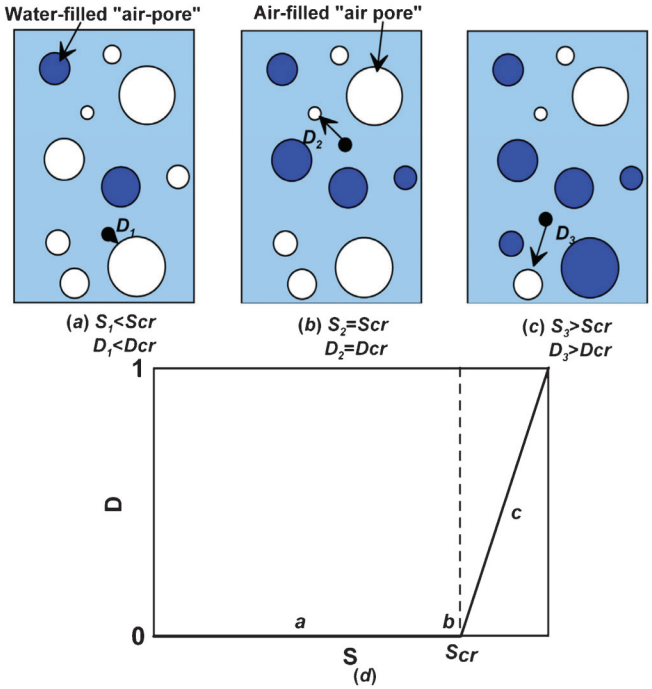

Figure 3.2 Schematic illustration of relation between degree of saturation with freeze-thaw damage (40,49).

saturation (S) is less than the critical degree of saturation (S_{cr}) as shown in Figure 3.2(a). However, the flow distance increases with the amount of absorbed water (or poor quality air void system), as does the degree of saturation. If either the critical flow distance or the critical degree of saturation is exceeded, frost damage initiates upon the next freezing cycle. The degree of damage can be quantified by the reduction in the dynamic elastic modulus of concrete as shown schematically in Figure 3.2(d).

In Figure 3.2(d) for all the values of degree of saturation below the critical degree of saturation the amount of damage (reduction is the elastic modulus) is very small. As soon as the degree of saturation exceeds the critical degree of saturation damage initiates in the Material (37,38,39,40,41).

It should be noted that the quality of air distribution and the volume of the air are two important parameters affecting the freeze-thaw resistance of the system. The quality of the air system is related to the critical flow distance while the quantity of the air voids (volume of air) is related to the critical degree of saturation. A fully saturated system, however, regardless of the quantity and quality of the air cannot even sustain a single freezing cycle without accumulating a significant amount of damage (42).

3.3 Background on Use of Acoustic Emission to Quantify Freeze and Thaw Damage

Acoustic emission (AE) is a nondestructive test method that is based on measuring the release of energy in concrete (e.g. the release of energy that occurs at the time of cracking). It should also be noted that AE can be performed in either a passive (i.e., capturing the acoustic wave generated due to formation of permanent defect such as crack) or active (i.e., using one transducer to generate a pulse and another transducer to capture the same pulse (in the simplest arrangement)). Classically AE is typically performed in passive mode in cement/concrete studies (52,53,54,55,56,57,58, 59,60,61,62,63,64,65,66). AE has been used in concrete to assess damage due to restrained shrinkage (53,54,55, 56,57) and mechanical loading (58,59,60,61,62,63,64, 65,66). AE has also been used to monitor freezing and thawing of mortar and it was observed that activity during both freezing and thawing (44,67).

In the present work, the evolution of damage in concrete during freeze–thaw cycles was monitored using both active and passive AE. The reduced relative dynamic elastic modulus was calculated for each cycle according to the transmitting time of waves using active AE. Passive AE was recorded to better understand the damage that develops during the freeze-thaw cycle.

3.4 Hypothesis and Outline for Experimental Investigation

There has been a great deal of debate on possible causes of joint deterioration in concrete pavements. It is the hypothesis of this work that the presence of water (or solution containing deicing salt solutions) in the joints plays a significant role in the deterioration of concrete pavement joints. First, it is hypothesized that joints can hold water or deicing fluids substantially longer than other parts of the pavement. This would enable the concrete at the joint to become preferentially saturated. The potential for a joint to hold water increases when the joint sealant is damaged or missing, at low spots in the pavement, and when the joint does not crack and open as designed (as has been noticed in the field). It is hypothesized that this propensity for saturation could make the concrete more susceptible to local freeze-thaw damage. Second, it is hypothesized that the use of air entrainment can increase the resistance to joint deterioration however it also believed that the use of air entrainment will not eliminate the potential for damage to occur. The addition of air entrainment is believed to extend the time required for the concrete to reach the critical degree of saturation.

While other factors can contribute to joint deterioration (e.g., the use of specific deicers, curing conditions, mixture proportions, construction details), they are not specifically considered in this paper. The scope of this paper is to examine the role of air entrainment on the rate of water ingress and degree of saturation increase in concrete. Second, this paper provides data to relate the degree of saturation to freeze-thaw damage in air entrained and non-air entrained concrete.

TABLE 3.1
Mixture proportions and constituent materials

Air content of paste (% by volume of mortar [a]/ concrete [b])	Cement (Type I) (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)
13 (6/4)	573.3	240.8	1333.3
22 (10/7)	548.9	230.6	1276.5
31 (14/9)	524.5	220.3	1219.8

[a]In calculating the equivalent air content in mortar it was assumed 45% paste by volume of the mortar;
[b]In calculating the equivalent air content in concrete it was assumed 30% paste by volume of the concrete.

3.5 Experimental Plan

This section describes mixture proportioning, specimen conditioning and the procedures of the testing in detail.

3.5.1 Mixture Proportions

Three mortar mixtures were prepared with different air contents (6, 10, 14% air by volume as measured in mortar). The air volume was calculated for an equivalent paste and concrete system respectively with the assumptions shown in Table 3.1. All specimens were made with ordinary portland cement (Type I) and had a water to cement ratio (w/c) of 0.42 which is typical of concrete pavements in the state of Indiana. Table 3.1 presents the proportions of the materials that were used.

Mixing was performed in accordance with ASTM C1585-04 (7). Two specimen geometries were used in this study: cylinders (25 mm height by 100 mm diameter) and prisms (25 mm by 25 mm by 125 mm). Cylindrical specimens were used for the water absorption test. The prisms specimens were used to evaluate the freeze-thaw damage development using AE. These specimens were cut from larger specimens.

3.5.2 Specimen Conditioning

The method of the specimen conditioning prior to water absorption testing can substantially influence the results of the test (69,70,71). If the specimen is not properly conditioned it can lead to a misunderstanding of the actual absorption behavior (21,69,70). Due to the significance of conditioning and necessity for the specimens to reach equilibrium the standard curing procedures were not used (48). The procedure that was used in this study allowed the specimens to equilibrate for a longer period.

The cylindrical specimens were cut 24 hours after casting from a larger cylindrical sample and sealed in two layers of plastic. The specimens were stored at 23 +/− 1°C for 28 days. After 28 days the specimens were removed from the plastic bag and placed in 50 +/− 1, 65 +/−1 and 80 +/−1% relative humidity (RH) environments where they were kept for more than a year to equilibrate. Table 3.2 lists the air content and relative humidity of each specimen.

3.5.3 Water Absorption

A procedure similar to ASTM C1585-04 (7) was used however the specimens were not conditioned following the accelerated ASTM testing procedure (described above). After conditioning, the outer circumference of the specimen was sealed with two layers of epoxy resin. After the epoxy hardened, the specimens were placed under water. Two small spacers were placed under the sample to provide a small gap between the bottom of the container and the lower surface of the sample. This allowed water absorption from both circular surfaces (Figure 3.3).

3.5.4 Freeze-Thaw Testing

This section describes specimen preparation and procedures used in freeze-thaw testing.

3.5.4.1 Specimen Saturation

The prismatic specimens were prepared to have different degrees of saturation before freeze-thaw testing was performed. The specimens were oven dried in steps to 105°C where they were maintained for 2 days. The specimens were then placed in a desiccator and evacuated to a residual pressure of 30mm Hg (4000 Pa) for 3 hours. After evacuation and while still under vacuum, water was introduced into the desiccators to cover the specimens. The specimens were left in the desiccators for 24 hours. This condition was considered

TABLE 3.2
Initial condition, air content and naming scheme for specimens used in the present study

Specimen name	Air content of the Paste (%)	Relative humidity (%)
50-13 [a]	13	50
65-13	13	65
80-13	13	80
50-22	22	50
65-22	22	65
80-22	22	80
50-31	31	50
65-31	31	65
80-31	31	80

[a]The first number shows the initial humidity of the specimen (e.g. 50-13 is 50% RH); The second number shows the air content of mortar of the specimen (e.g. 50-13 is 13% air by volume of paste).

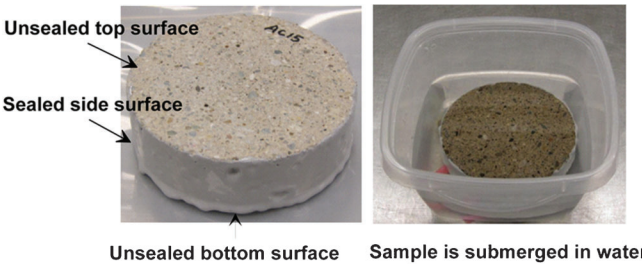

Figure 3.3 Double sided sorption test of specimen with 1-inch thickness

as saturated (i.e., 100% degree of saturation). The degree of saturation was reduced for some specimens (i.e. 0.96, 0.92, 0.90, 0.86, 0.82, and 0.78) by short periods of drying at 23℃ and 50% relative humidity. During the drying period the mass of the specimens was closely monitored. After drying all the specimens were sealed in plastic bags for a minimum of 3 days to allow moisture to re-distribute before freezing and thawing testing.

3.5.4.2 Preparation of the Specimen for Freezing and Thawing

Figure 3.4 shows the procedure used for preparing the specimens for AE testing during freeze-thaw cycles. The specimens were first preconditioned to different degrees of saturation as described in section 3.5.4.1. After preconditioning the specimens were wrapped with a thin plastic sheet as shown in Figure 3.4(*a*). The thin plastic sheet was used to protect the sample from further drying during the handling. The specimens were then sealed with a "heat shrink wrap" to further protect the specimens against moisture exchange with surroundings (prevent them from absorbing or releasing water during the freeze-thaw process) as shown in Figure 3.4(*b*). It is important to note that the "heat shrink wrap" was in loose contact with sample (with the exception of the specimen ends) so that the specimen can expand freely during the test while minimizing any restraint.

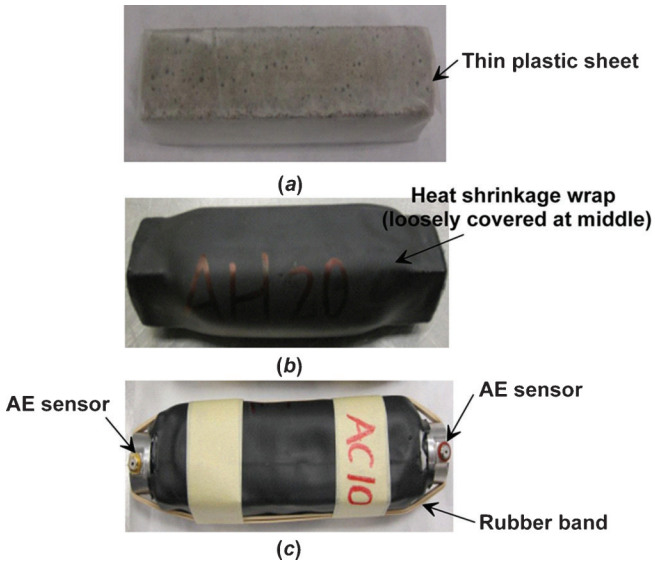

Figure 3.4 Specimens prepared for acoustic emission testing during freeze-thaw cycle: (*a*) thin plastic sheet to avoid evaporation during specimen preparation and handling (*b*) specimen covered by heat shrinkable wrap to avoid evaporation during specimen preparation and handling

The AE sensors (transducers) were attached on the two ends with a thin layer of vacuum grease as shown in Figure 3.4(*c*). Figure 3.5 shows that all the specimens were placed on a suspended base in testing to minimize noise/vibration transmission from surrounding environment. The threshold was set at 60 dB and 34 dB for active and passive AE, respectively. Testing was also performed on dry specimens to ensure that sounds were not being recorded from the environment, freezing unit, or coupling agent (72).

3.5.4.3 Temperature Cycle used for Freeze-Thaw Testing

Figure 3.6 shows the temperature cycle (in air) which allows one cycle per day. Temperature was controlled to vary from 10 +/− 1℃ to −18 +/− 1℃. The rate of

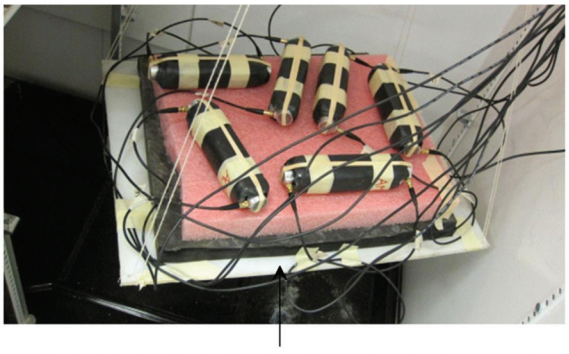

Figure 3.5 Specimens placed on a suspended base to eliminate vibration and noise from surrounding environment (inside of freeze-thaw chamber)

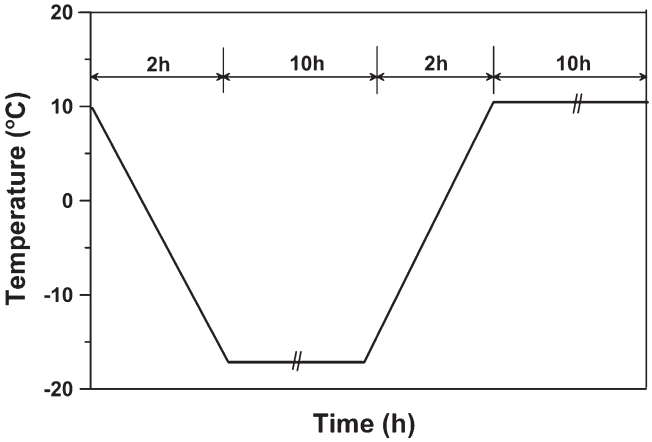

Figure 3.6 Temperature cycle used in freeze-thaw experiment (air temperature)

the temperature change was 14°C/hour resulting in a 2-hour transition period and two 10–hour periods at 10 +/−1 °C and −18 +/−1 °C respectively.

3.6 Experimental Results and Discussion

3.6.1 Water Absorption

3.6.1.1 Sorptivity

The amount of absorbed water (I) is normalized by the cross-sectional area exposed to water as outlined in standard (7):

$$I = \frac{m_t}{a \cdot d} \tag{3.1}$$

Where:

m_t = the change in specimen mass at time t in grams;
a = the area of both sides exposed to water, in mm^2;
d = the density of water in g/mm^3.

Sorptivity is defined as the slope of the water absorption versus square root of time curve (7). The initial sorptivity is the slope of this curve within the first 6 hours, while the secondary sorptivity is the slope of the curve between 1 to 8 days.

Figure 3.7(*a*) illustrates the sorption results for the specimens conditioned at 50% RH with 13% and 31% air contents by volume of paste. The specimens show a similar sorptivity (slope of the curves) and amount of absorbed water initially; however, over time the specimens with higher volumes of air absorb more water. This occurs since the air voids provide space for water (73,74), however, the diffusion of air and the over-pressure in the air-bubbles delays water absorption which corresponds for the long time to saturation (40,75,76). It should be noted that although the secondary sorptivity for sample with higher air content is higher, this sample requires absorbing more water to reach the critical degree of saturation.

Figure 3.7(*b*) shows the water absorption results for specimens conditioned at 65% RH. Comparing this result with Figure 3.7(*a*) suggests that the amount of absorbed water for the specimens conditioned at 65% RH is lower than that of specimens conditioned at 50% RH with the same air content. Figure 3.7(*c*) shows the absorption for specimens conditioned at 80% RH.

The specimens at 65% RH and 50% RH show a nick-point (point where the curve changes slope) at the end of the 6 hours on a water absorption square-root of time curve however, the nick-point cannot be seen on the results of 80% RH and a more gradual rate of absorption can be seen.

The relative humidity in which the specimens were conditioned in has a significant impact on the results (69,70,71). The driving force of unsaturated fluid transport is the capillary suction (11,78,79). When samples are in equilibrium with a lower relative humidity a larger volume of pores are empty and available to be filled with water during the water sorption. Furthermore, at lower humidity, the maximum size of the pores

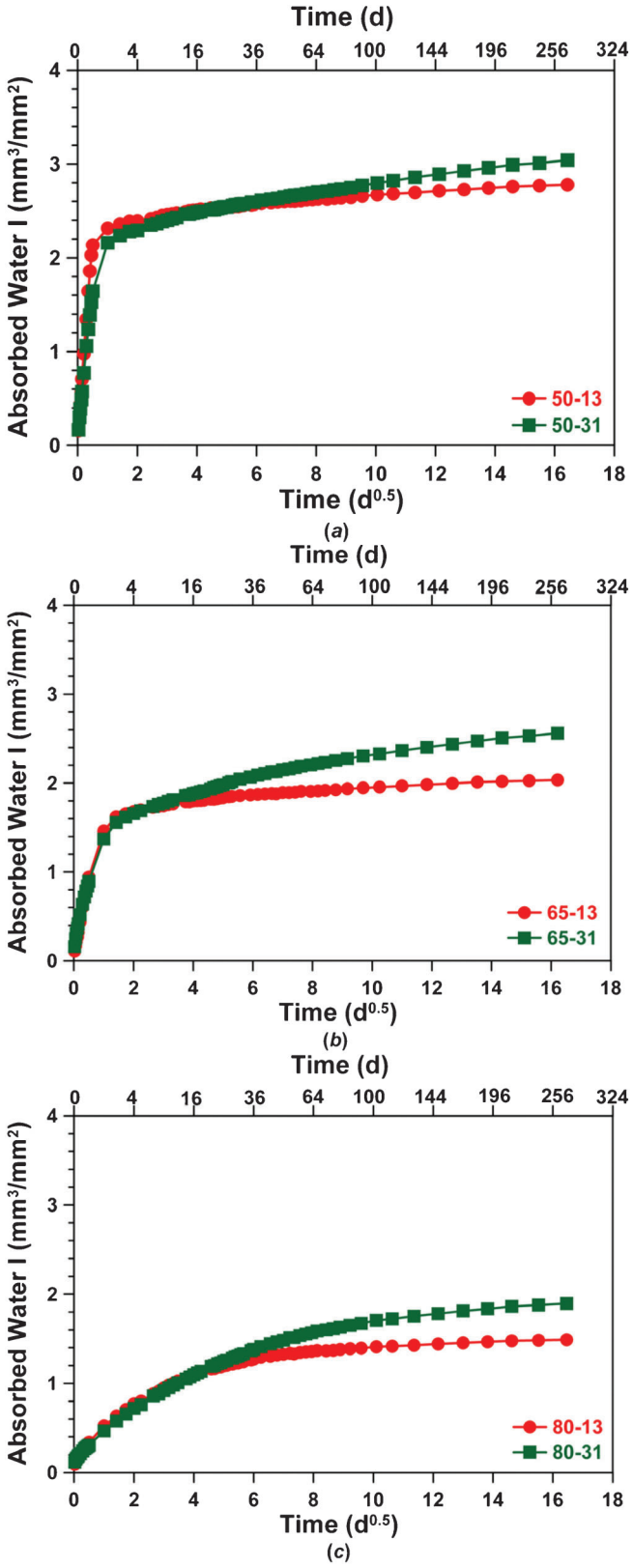

Figure 3.7 Effect of air content and initial moisture on water absorbed: (*a*) 50% RH (*b*) 65% RH (*c*) 80% RH

that is filled with water is smaller, creating a higher suction force. The overall effect will be higher rate of water absorption and high volume of absorbed water.

3.6.1.2 Degree of Saturation

Figure 3.8(*a*) shows that the degree of saturation (*S*) of the specimens conditioned at 50% RH with two air contents (13 and 31% by volume of paste). Note that the degree of saturation is plotted as a function of square-root of time on the lower x-axis while actual time is shown on the upper x-axis.

The most striking feature of the graphs in Figure 3.8 is the fact that the degree of saturation decreases with increasing air content. At the end of the initial 6-hour sorption period samples with lower air content show higher degree of saturation. For samples equilibrated at 50% RH the degree of saturation is 39% less when the air content increases 10%, the decrease in degree of saturation for samples equilibrated at 65% and 80% RH is 23% and 26% respectively.

Note that the secondary rate of absorption (Figure 3.7) is different for samples with different air content; however, in Figure 3.8 the secondary rate of increase in degree of saturation is approximately the same for materials with different air content. This suggests that for an equal time of exposure to water, the specimen with the higher air content has a lower degree of saturation (40,75,76).

The secondary rate of increase in degree of saturation can be fitted with a linear function to estimate the amount of absorbed water over a long period of time. The linear fit used in Figure 3.8 is shown with a solid line. Since the objective here is to estimate the degree of saturation over a long period of time only the date between 100 to 240 days is used in fitting this straight line. Using this linear function the time to reach the critical degree of saturation is calculated for each specimen with different air content and initial equilibrium condition and reported in Table 3.3.

3.6.2 Freeze-Thaw Testing

3.6.2.1 Monitoring the Damage Development Using Active Acoustic Emission

The relative dynamic elastic modulus is frequently used as an index to evaluate the extent of damage (36,37,38,39,40,41,42,43,44). Using active AE the transmission time of a single pulse was measured along the sample. The transmission time along the length of the sample was measured in both directions (i.e., from sensor 1 to 2 and from sensor 2 to 1). The transmission time was measured three times in each direction and the average transmission time is reported here (average of 6 values). The transmitting time was measured after each cycle when the temperature was stable at 10℃ for a minimum of 2 hours.

The relative elastic modulus, i.e. E_l/E_o is square proportional to the velocity of wave transmitting through materials, which is inversely square proportional to the ratio of the wave transmission times (80), as shown in Eq. 3-1. Damage parameter (D) can also be

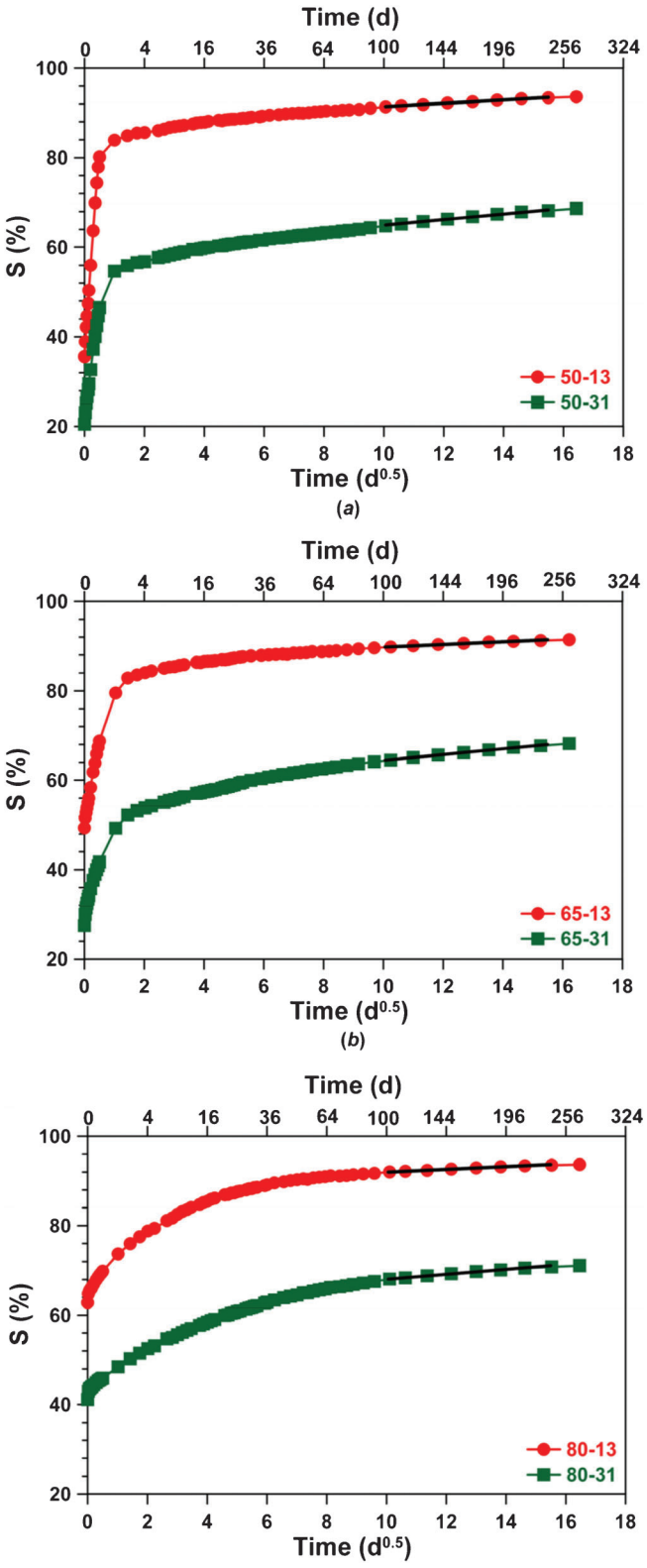

Figure 3.8 Results of sorption test provided as increase in the degree of saturation: (*a*) 50% RH (*b*) 65% RH (*c*) 80% RH

TABLE 3.3
Time to reach to the critical level of saturation (88%) for the specimens with different air content

Initial relative humidity (%)	Air content by volume of paste (%)	Secondary sorptivity ($mm^3/mm^2.d^{0.5}$)	Time to reach the critical degree of saturation (88%) (S_{cr}) in years (+/−1.7%)
50	13	0.485	0.011 (4d)
	22	0.691	5.08
	31	0.750	6.10
65	13	0.368	0.016 (6d)
	22	0.513	5.63
	31	0.785	5.90
80	13	0.563	0.015 (5d)
	22	0.606	4.00
	31	1.009	5.82

estimated using Eq. 3-2.

$$D = 1 - \frac{E_t}{E_o} = 1 - \left(\frac{T_o}{T_t}\right)^2 \qquad (3.2)$$

Where:

E_o, T_o = the dynamic elastic modulus before freeze-thaw testing began and corresponding transmitting time;

E_t, T_t = the dynamic elastic modulus during testing at any time t and corresponding transmitting time.

It should be noted that the main cracks were along the direction of wave propagation and as such the wave is least sensitive to these cracks however the damage was still easily recorded.

Figure 3.9 illustrates the damage index (Eq. 3-2) with increasing cycles of freezing and thawing. The damage initiates during the first cycle when the degree of saturation is above 86~88%. The specimens with lower degree of saturation do not show damage while specimens with a higher degree of saturation show a rapid deterioration. It can be seen that the saturated specimens (S=100%) can not sustain more than 3 cycles before complete failure occurs.

Figure 3.10 shows the rate of damage (dD) development per freeze-thaw cycle (dN) (as determined by the slope of Figure 3.9) for specimens with different degrees of saturation. A critical degree of saturation appears to occur at approximately 86 – 88%. The critical degree of saturation appears to be independent of the air content.

3.6.2.2 Acoustic Energy Measured Using Passive Acoustic Emission

Figure 3.11 shows the amplitude of the acoustic events as a function of time for a specimen with 96% degree of saturation and 13% air content during freezing cycle. The temperature is the temperature measured in the center of the mortar specimen. Figure 3.11(*a*) illustrates the amplitude distribution for the first freeze-thaw cycle and Figure 3.11(*b*) illustrates the amplitude distribution during the second freeze-thaw cycle for the same specimen.

In Figure. 3.11(*a*) the acoustic events begin to occur as the temperature of the specimen decreases. A cluster of acoustic event is shown in Figure 3.11(*a*) as highlighted by the ellipsoid. This cluster of data is not seen in Figure 3.11(*b*). These events can be attributed to micro-cracking of the specimen due to thermal loading which may be a result of temperature gradient or a result of thermal expansion coefficient mismatch between the paste and aggregate. Since the thermal loading is not changed during the second cycle, the

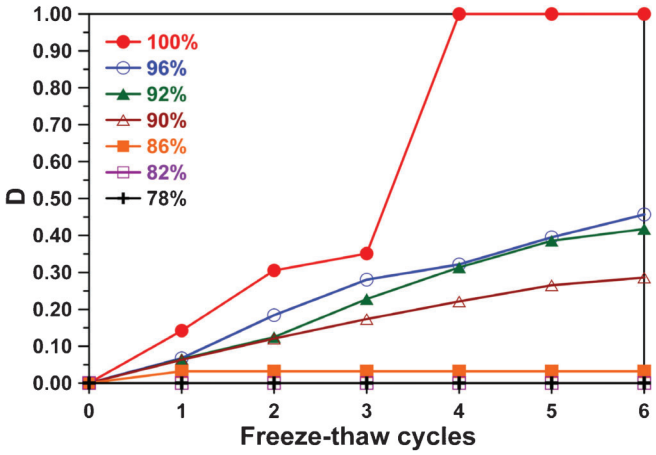

Figure 3.9 Decrease of the relative dynamic elastic modulus with freeze-thaw cycles

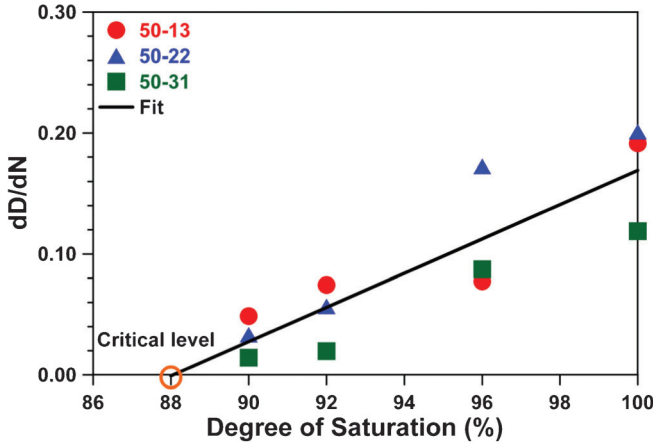

Figure 3.10 Rate of decrease of relative dynamic elastic modulus with degree of saturation

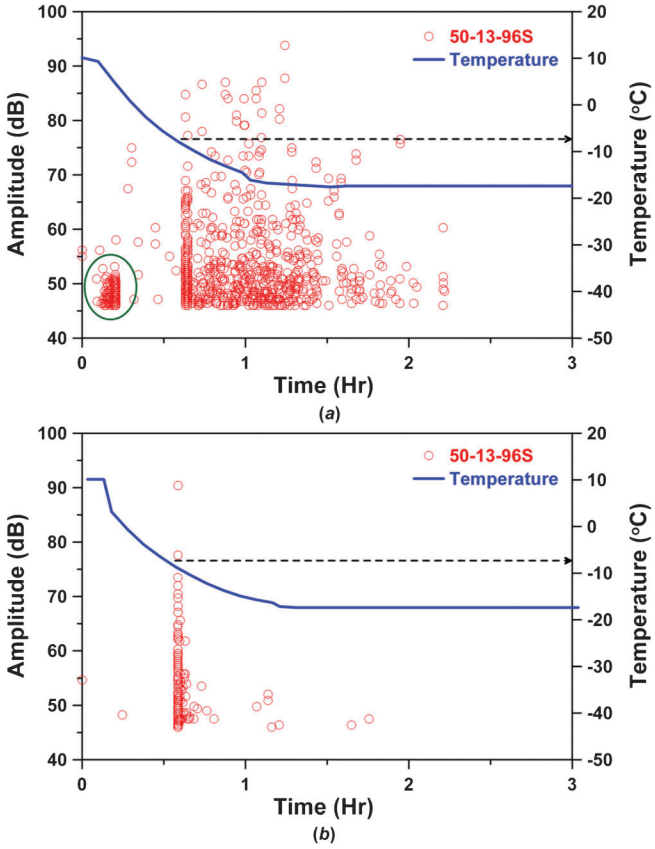

Figure 3.11 Amplitude in the transition time of freezing (96*S*): (*a*) first cycle (*b*) second cycle

damage due to thermal loading does not exceed the previous level of damage in materials and additional cracking would not be expected (80).

In Figure 3.11 the acoustic events begin to increase dramatically after the temperature drops below −8℃ in both cycles. The number of events is higher in the first cycle compared to the second cycle as more cracking would be expected in the first freeze-thaw cycle while these cracks would be expected to extend in the following cycles. The damage at the point (below −8℃) is likely attributed to formation of ice and cracking inside the specimen. This is consisted with the observation that pore solution freezes below 0℃ due to pore confinement and dissolved ions in pore solution (81,82,83).

3.6.2.3 Desorption Isotherm

Figure 3.12 shows the desorption isotherm for the specimens with 13% and 31% air content by volume of paste. The desorption curve demonstrates the mass of water lost from the specimen at each relative humidity step (i.e., different pore sizes begin to empty out at different relative humidities starting with large pores at high relative humidities and smaller pores at lower humidities). The profile of the desorption curve is similar for both specimens until high relative humidities, i.e. 97.5% RH. At relative humidities higher than 97.5%, a larger difference of the porosity can be seen.

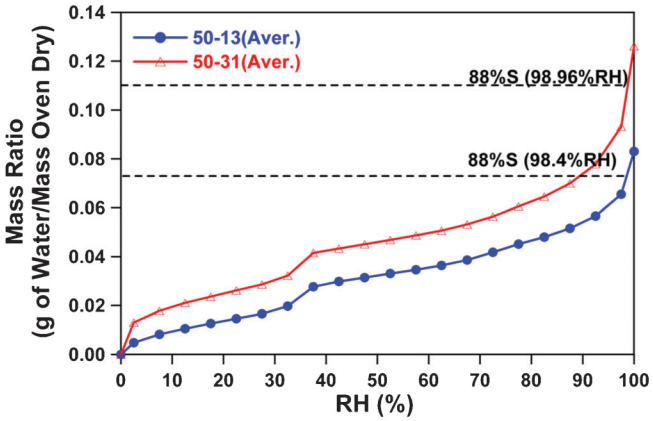

Figure 3.12 Mass change at decreasing RH containing deionized water

This difference corresponds to the air entrained porosity.

The critical degree of saturation (88%) corresponds to relative humidity of 98.4% for specimen with 13% air content and 98.96% RH for specimen with 31% air content, respectively. This implies that some of the air entrained pores are water filled when the specimen is at or above critical degree of saturation. The difference in mass loss between the 13 and 31% air content at 2.5% RH is currently unknown however this is repeatable between specimens.

3.7 Calculated Time to Reach the Critical Degree of Saturation

In section 3.6.1 the rate of absorption of water and its relation to the degree of saturation was discussed and in section 3.6.2 the influence of the degree of saturation on freeze-thaw damage was discussed. To better understand how these findings can be related to one another to predict the time to freeze-thaw damage a linear function was fit to the plot of degree of saturation verses square root of time data (using the secondary absorption).

Table 3.3 shows the time required for each specimen equilibrated at different initial condition to reach the critical degree of saturation (i.e., 88% in this study). Specimens without air entrainment can reach to the critical degree of saturation within days (4~6 days). The use of air entrainment raised the air content, and decreases the degree of saturation. This increases the time to reach a critical degree of saturation to 3~6 years. The rate of water absorption is substantially different in the systems with entrained air compared to non-air entrained systems.

3.8 Conclusions

The water absorption of mortar containing different volumes of entrained air was examined in this study. While tests like ASTM C 1585-04 (7) can be used to provide an index of water absorption, the differences between non air entrained and air entrained systems

were small when only mass gain was investigated. While the absorption rates in plain and air entrained systems were similar initially the air entrained system showed a higher rate of ingress at later ages. By normalizing the results of water absorption in terms of the degree of saturation a clear distinction between the non-air entrained and air entrained mixtures can be made. While the non-air entrained system took 4 to 6 days to reach 88% saturation, the air entrained system is estimated to require approximately 3 to 6 years. This shows that entrained air will substantially increase the time to failure.

The damage due to freeze-thaw was monitored using both passive and active AE. A critical degree of saturation was observed with specimens that have a degree of saturation greater than the 86 to 88% exhibiting damage during the few freeze-thaw cycles.

The critical degree of saturation appears to be independent of the air content as materials with a degree of saturation above the critical degree undergoing damage after a few of freeze-thaw cycles irrespective of the air content. The volume of air and quality of the air void system however likely has a strong relation to the critical flow distance.

Increasing the air content resulted in a longer time for the mortar to reach to the critical degree of saturation. While increasing the air content can delay the time freeze-thaw damage initiates in practice; it appears that increasing of the air content cannot eliminate the potential for freeze-thaw damage.

3.9 Acknowledgements

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CHAPTER 4: EVALUATING SOY METHYL ESTER PENETRATING CONCRETE SEALERS

The majority of deterioration that occurs in concrete can be related to fluid transport. In many cases reducing the infiltration of fluids into the pore system of the concrete can make the concrete more resistant to deterioration. The resistance to fluid ingress can be altered by changing mixture proportions, curing conditions, or through the use of a topical sealant. Soy Methyl Ester polystyrene (SME-PS) blends are penetrating sealants that are derived from soy beans. SME-PS has shown the ability to reduce fluid absorption in concrete when the SME-PS is used as a topical sealant. This paper describes a series of experiments that were developed to evaluate the effectiveness of various dosage rates of SME-PS at increasing concrete durability by reducing fluid ingress and reducing the potential for freeze-thaw damage.

4.1 Background

Concrete pavements have a reputation for providing good long-term performance, however a portion of these pavements have recently shown premature joint deterioration. This joint deterioration compromises the performance and potential service life of an otherwise healthy pavement. This type of damage is frequently seen as either the development of cracking parallel to the joint or spalling and cracking at the joint from the bottom of the saw cut to the surface of pavement approximately 4 to 6 inches from the joint. During field inspections it has been observed that where the joints are damaged the joint sealant is damaged and the joint contained standing water (or fluid containing water and deicing salts). Research is needed to better understand the mechanisms responsible for this damage since it appears to occur in both poorly air entrained and properly air entrained concrete.

Figure 4.1 illustrates a typical longitudinal joint in a concrete pavement that is used in the state of Indiana. A three step process is used to create the joint. First, a sawcut is placed in the pavement to 1/3 of the pavement depth to control random cracking. This joint typically causes a crack to form directly below the saw cut and the joint opens. To allow the joint to open, sometime is typically allowed to expire between the time that the first saw-cut is placed and the time that a second cut is placed (approximately 1 inch deep) to widen the saw cut near the surface. By allowing the pavement to crack and open before the second cut is placed the joint width can be made more uniform from panel to panel. The third step involved placing a backer rod in the joint to

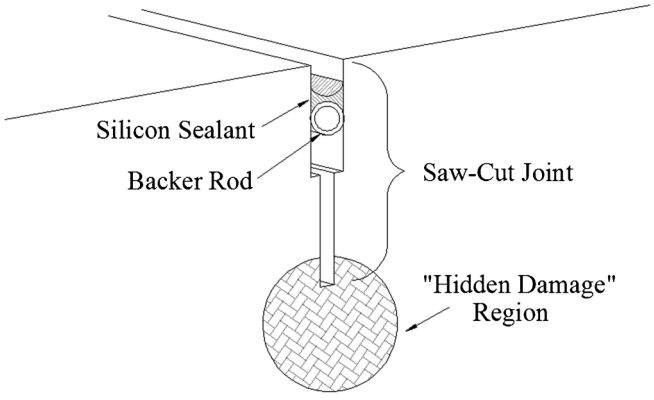


Figure 4.1 Typical D-1 Contraction Joint (84)

keep the sealant at the top of the joint. A joint sealant is placed on top of the backer rod and the joint sealant adheres to both sides of the widened saw cut. The sealant is thought to be necessary to keep water and incompressible materials out of the joint. A typical method for sealing joints is to use a silicon sealant.

If the joint sealant remains intact, it will keep water and solutions containing deicing salts out of the joint. However, this sealant frequently becomes damaged and the geometry of pavement joints provides a place for fluid to collect. This fluid will be absorbed by the concrete and can lead to freeze-thaw damage. In addition to this, the fluid can introduce deleterious substances into the concrete which can cause the concrete to degrade (85). The irony is that while the damaged joint sealant may not prevent fluid from getting into the crack, it will substantially reduce the potential for water to evaporate from the joint.

An alternative to the use of silicon joint sealant systems are topical sealants that penetrate the pores of the concrete. Unlike the silicon sealant which forms a physical barrier on the surface of the concrete, these sealants are absorbed into the pore system creates a hydrophobic layer which inhibits the ingress of water. It should be noted that unlike the silicon sealants, the penetrating sealants do not have the ability to keep incompressible objects out of the joints.

Recent research has shown the potential for using plant-oil based products as concrete sealants (86). One of these products is Soy Methyl Ester (SME). SME also has the potential to be both an effective and environmentally friendly concrete sealant. Previous research has shown that when treated with SME or SME-PS blends the water absorption of the concrete is dramatically reduced (87). The focus of this research is evaluating the effectiveness of SME-PS sealants at increasing the durability of concrete, especially in a freeze-thaw environment.

4.2 Research Program Overview

This work is intended to evaluate the effectiveness of SME-PS sealants on concrete durability. Specifically the influence of penetrating concrete sealants is evaluated as it related to water absorption, freeze-thaw durability, and the ingress of chlorides ions. A complete overview of the testing program can be seen in Table 4.1.

4.2.1 Materials

ASTM C150 (AASHTO M 85) Type I ordinary portland cement (OPC) was used for this study. The mortar mixtures contained cement with a Blaine fineness of 476 m^2/kg, a specific gravity of 3.15, and an estimated Bogue compositions of 52% C_3S, 18% C_2S, 8% C_3A, 9% C_4AF, and a Na_2O equivalent of 0.5. The fine aggregate used for the mortar was natural river sand with a fineness modulus of 2.71, an apparent specific gravity of 2.58, and absorption of 1.8%. The mixture proportions were adjusted for aggregate absorption. The mortar mixtures in this study were prepared in accordance to ASTM C192-06 (68). Prior to mixing all aggregates were oven dried and allowed to cool for 24 h. Both the water and cement were conditions at room temperature for a minimum of 24 h.

The fine aggregate used for the concrete was natural river sand with a fineness modulus of 2.71, an apparent specific gravity of 2.77, and absorption of 1.47%. The coarse aggregate was a # 8 ASTM stone with an apparent specific gravity of 2.742 and absorption of 1.4%. A polycarboylate-based high-range water-reducing admixture (HRWRA) was used in some of the mixtures to allow for a consistent workability. Air entrained admixture and retarder admixture were added to the concrete mixtures.

4.2.2 Mixture Proportions

One concrete mixture and three mortars mixtures were used in this study. The concrete mixture that was used for these tests was a typical INDOT class C bridge deck concrete. The concrete was prepared with a *w/c=0.40* with 28% fine aggregate and 38% coarse aggregate. The mortars were prepared with 55% fine aggregate and with water-to-cement ratios (*w/c*) of 0.42,

TABLE 4.1.
Testing Program Overview

Test Description	Test Methods	Mixtures*	Topical Sealant
Water Absorption	ASTM C1585	M42	SME – PS (2 doses) Solvent Based Silane Water Based Silane
Concrete Freeze-Thaw Durability	ASTM C666 (A)	M45	SME – PS (2 doses) Solvent Based Silane
Durability of Sealers under Freezing and Thawing Conditions	ASTM C1585 (Modified)	C40	SME – PS (2 doses) Solvent Based Silane Water Based Silane
Chloride Ingress	Visual Observation	M42	SME – PS (2 doses) Solvent Based Silane Water Based Silane

*Mixture Proportions Defined in Table 4.2

TABLE 4.2.
Mixture Proportions

Material	C40	M42	M45	M47
Cement (kg/m^3)	316	609	586	571
Class C Fly Ash	60	–	–	–
Water (kg/m^3)	150	256	264	268
Fine Agg. (kg/m^3), SSD	736	1444	1444	1444
Course Agg. (kg/m^3), SSD	1049	–	–	–
Air entrain admix (ml/100kg cem.)	20	–	–	–
Retarder admix (ml/100kg cem.)	98	–	–	–
HRWRA (g/100g cem)	0.5	–	–	–

0.45, and 0.47. A complete list of mixture proportions can be found in Table 4.2.

4.2.3 Concrete Sealants

During this testing program, samples were tested both with and without treatment of a topical sealant. Three different sealants were tested. The first is Soy Methyl Ester blended with 5% polystyrene by mass. The results from the SME-PS treated samples were compared to two commercially available silane sealants. The first is a solvent-based alkyalkoxysilane sealer (SBS) with greater than 50% active ingredients. This sealant is a solution of silane dissolved in an isopropanol solvent. The second commercially available sealer is a water-based alkyalkoxysilane penetrating sealer (WBS) that consists of 40% silane. This sealant is an emulsion of silane in water.

4.3 Penetration of SME into Concrete

In order to be able to optimize the use of SME-PS sealants, it is important to understand how it behaves when it is applied to the concrete. The first step in this study was determining the influence of various factors on the penetrability of SME. Specifically being studied are the influence of concrete moisture, size of polystyrene molecules, and time. By understanding this concept, specifications can be written so that contractors can apply this treatment in the most economical way.

4.3.1 Influence of Concrete Moisture on SME Penetration

The influence of concrete moisture on SME penetration was tested on concrete samples. A series of 100 mm $\times$ 200 mm cylinders were cast of mixture C40. After 24 hours the cylinders were demolded and sealed in double plastic bags at 23 $\pm$ 0.5 ℃ until the samples reached an age of 28 d. After 28 days of curing the cylinders were removed from bags and three 50 mm $\pm$ 2 mm thick samples were cut from the central portion of each cylinder with a wet saw. After cutting, samples were conditioned by placing them in environmental chambers at 23 $\pm$ 0.5 ℃ and at three different relative humidities (50$\pm$1%, 65$\pm$1% and 80$\pm$1%) for 18 months before testing.

After the 18 months, the sides of the sample were sealed with epoxy and a plastic mold was placed around the sample to prepare a dam. The edge between the plastic mold and the concrete sample was sealed using silicone, which was allowed to dry for 24 h. The mass of the samples was then recorded. About 20 g of SME sealant were placed in the dam. After 48 h, the additional sealant was removed from the dam and the mass of the sample was recorded.

Figure **4.2** shows both the absorption of sealant and water after 48 h. The samples were then cut vertically using a wet saw, for a direct visual measurement of the sealant penetration (Figure 4.3).

Figure **4.2** and Figure 4.3 show that the moisture content of the samples has a high influence in the penetration of the sealant.

4.3.2 Influence of Polystyrene Chain Length on SME Penetration

Although SME is an effective sealant by itself, its high solvent capacity enables it to be blended with polymers such as polystyrene (86). By blending the SME with PS, it is possible to tailor the properties of the solution for a specific need (87). Another benefit of using a SME-PS blend is that the waste polystyrene, which otherwise would be put in a landfill, can once again be useful. If waste PS is to be used, it is important to understand how different sources of polymer would affect the final product. In this study, the effect of PS chain length on sealant penetration was tested.

Penetration of SME sealants blended with PS of different size polymer chains was tested on mortar samples which were cast on 35 mm $\times$ 300 mm cylinder

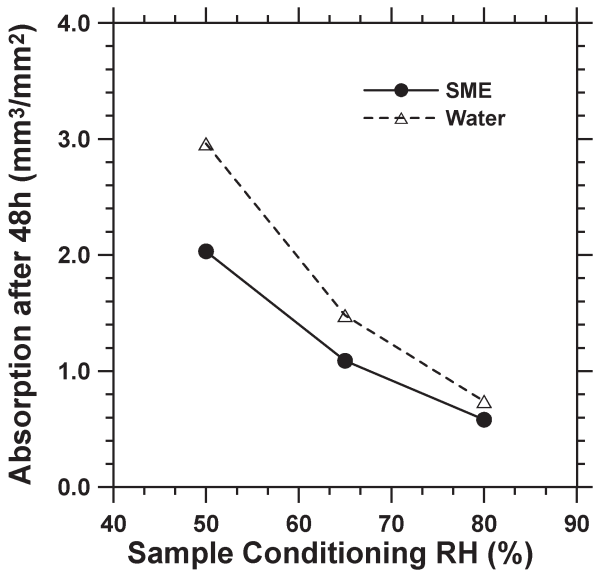
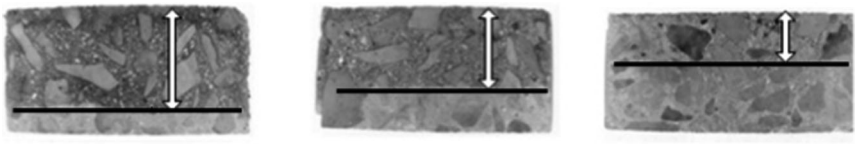


Figure 4.2 Volume of SME and Water Absorbed after 48h by Concretes Conditioned at Various Relative Humidities



a) 50% RH b) 65% RH c) 80% RH

Figure 4.3 Visual Observation of SME Penetration (from top) into Concretes with Different Levels of Saturation after 48h. SME Penetration is Highlighted in Black. Sample Cross-section is 5cm by 10cm

molds, where they were kept until the age of 28 days. Then, samples were demolded and 50 mm $\pm$ 2 mm thick samples were cut from the central portion of each cylinder with a wet saw. After cutting, samples were conditioned by placing them in environmental chambers at 23 $\pm$ 0.5 ℃ and 65 $\pm$ 1% relative humidity for 8 months before testing.

After the 8 months, the sides of the sample were sealed with epoxy. After the epoxy had hardened, aluminum tape was placed around the sample to prepare a dam. The edge between the aluminum tape and the mortar samples was sealed using silicone, which was allowed to dry for 24 h. The mass of the samples was then recorded. About 5 g of sealant were placed on the dam and allowed to absorb. In this experiment four SME-PS blends were tested: No PS (pure SME), M_W 2,400 PS, M_W 44,000 PS, and M_W 382,100 PS. Each of these molecular weights corresponds to the chain length of the polystyrene molecules. Each of the SME-PS blends were prepared with 5% PS by mass. After 48 h, the sealant was carefully removed and samples were cut vertically using a wet saw, for a direct visual measurement of the sealant penetration (Figure 4.4). Results show that the presence of PS influenced the ability of the sealer to penetrate the samples. As the molecular weight of the PS increases the penetration depth of the sealer decreases.

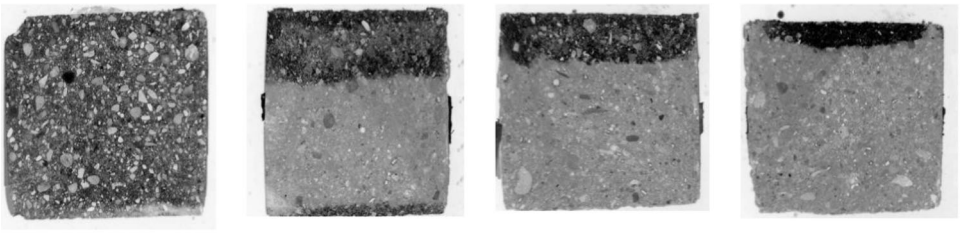
4.3.3 Influence of Time on SME Penetration

This test investigated the effect of time dependency on the penetration depth of SME-PS. To perform this study, six 2.5cm $\times$ 2.5 cm $\times$ 10 cm prisms of mixture M47 were prepared. These samples were demolded at 24h and allowed to dry at 23℃ and 50%RH for seven days prior to being submerged in SME-PS containing a fluorescent dye (0.5% by mass). At certain time intervals the samples were removed from the solution. These samples were cut with a small wet saw and photographed under an ultraviolet light to determine the penetration depth of the SME-PS. Both images of the SME-PS penetration and a graphical display of penetration depth over time can be seen in Figure 4.5.

4.4 Water Absorption

The sealants ability to prevent water absorption into concrete was measured using ASTM C1585-04 [ASTM, 2004]. The sealants being tested are SME-PS (2 dosages), solvent based silane, and water based silane. Samples were prepared as 4x8 cylinders of mixture M42. Samples were demolded at 24h and sealed in a double plastic bag for 14d. At this time each cylinder was cut into three 5 cm tall discs. The top and bottom 2.5 cm of the cylinder was discarded. The cylinders were allowed to condition at 23℃ and 50% RH for 6 month prior to the application of the sealants. SME-PS was applied to cylinders by submerging the exposed face in the SME-PS for 6h (Dose 1) and 24h (Dose 2). The SBS and WBS were applied evenly with a paint brush on the exposed surface. Results of the water sorption test can be found in Figure 4.6.

The application of each of the sealants tested resulted in a reduction in the amount of water absorbed into the samples. Both silane sealants were more effective at reducing water absorption than the SME-PS. At seven days the volume of water absorbed in the silane sealants was reduced by 95% while the SME-PS samples were reduced by approximately 88%. Another observation is that the effectiveness of the sealant slowly diminishes over time. After 28ds the reduction in water absorption was reduced to 90% and 77% for the silane and



a) SME Only b) M_W 2,400 c) M_W 44,000 d) M_W 382,100

Figure 4.4 Penetration Depth of SME-PS Blends Highlighted in Black (penetrating from top surface only). Each Sample was Treated with a SME-PS Blend Prepared with Polystyrene of Various Chain Lengths. Samples are 35 mm by 50 mm in Cross-section

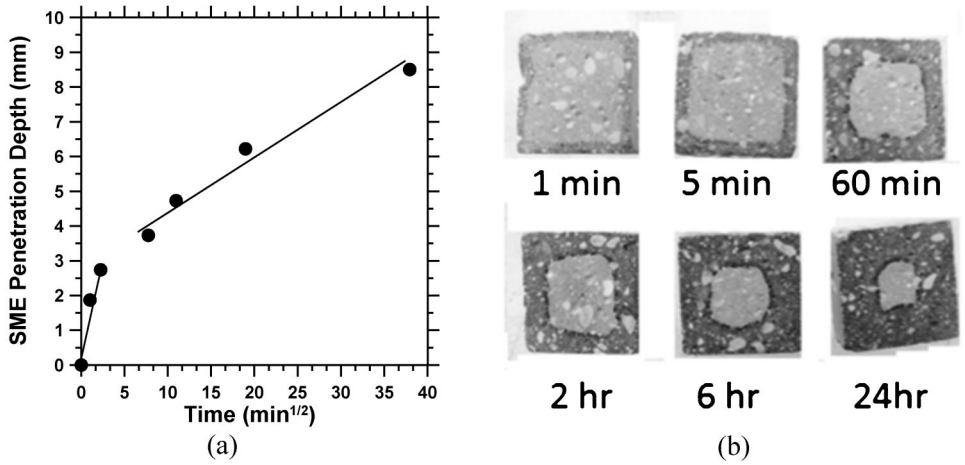


Figure 4.5 Penetration of SME into 2.5 cm Square Samples. (a) penetration depth vs. time, (b) SME-PS highlighted in black. Top Row: 1min, 5min, 60min. Bottom Row: 2h, 6h, 24h

SME-PS respectively. Although the sealants allow the water to continue to ingress into the samples for longer times, the volume of water absorbed is still less than the untreated samples.

4.5 Freeze-Thaw Durability

When porous materials such as concrete contain water, they become susceptible to damage from freezing and thawing cycles (85). This degradation is further enhanced when the water contains aggressive ions such as chlorides (88). A common method for improving the freeze-thaw durability of concrete is through the use of air entraining admixtures (AEA) (85). Increasing air content of concrete increases the freeze-thaw durability by providing space for water expansion and making it more difficult to saturate the concrete. Although normally effective, it is not always possible to use AEAs. As an example, fly ash can interacts with AEAs and render them ineffective at increasing the air content of concrete. One alternative method for improving freeze-thaw durability is through the use of topical sealants.

4.5.1 Cold Weather Behavior of SME-PS

When a material reaches its freezing/melting point it undergoes a phase transition between liquid and solid. In the case of pure water, a change in temperature from 1℃ to 0℃ will result in a phase transition of the entire

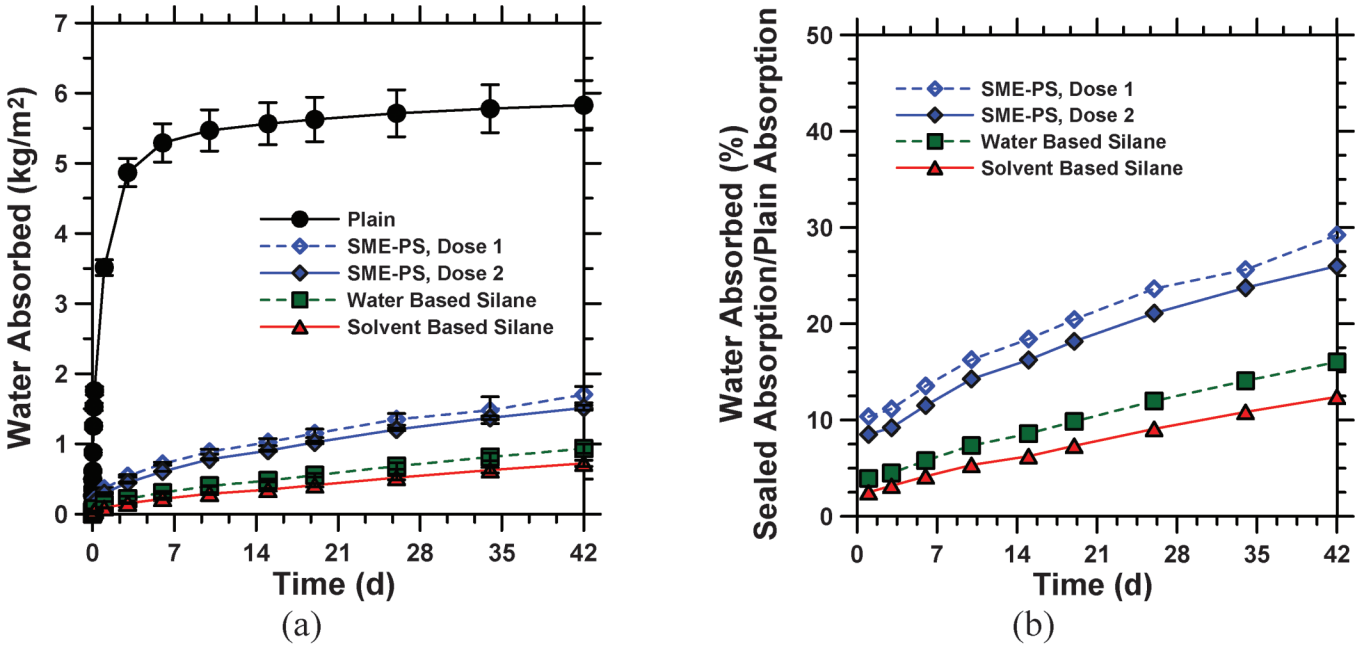


Figure 4.6 Water Absorption Experimental Results. water absorbed (b) reduction in water absorption

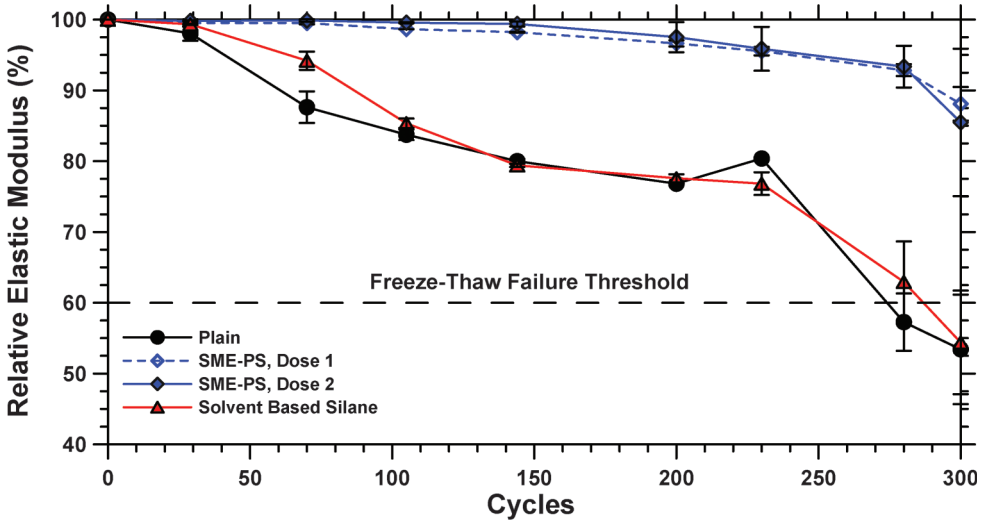


Figure 4.7 Freeze-Thaw Experimental Results, Relative Elastic Modulus

system. SME does not behave in this same manner. Unlike water which can be considered a single-phase liquid, SME is a solution of different fatty acid methyl esters (FAME). Each of these FAMEs have their own unique temperature in which they will change phase.

When a critical temperature is reached, FAMEs will begin to lose their solubility and come out of solution. This will result in a second solid phase forming in the solution. These solids are conglomerations of waxy crystals that will give the solution a cloudy appearance. The temperature at which this first occurs is known as the cloud point. For SME, this value is typically accepted as 0℃ (8,9). The cloud point of SME-PS with 5% and 10% PS was measured to be 5℃ according to ASTM D2500 (10). It can be speculated the PS is losing its solubility at this temperature.

As the temperature continues to drop below the cloud point, more of the FAMEs will fall out of solution and precipitate into waxy solids. Eventually there will be enough solidification that the solution will lose its ability to flow like a liquid. This point, known as the pour point, SME becomes a gel-like substance. This temperature is typically accepted as −4℃ (89). The cold flow properties of SME are one of the major draw backs of using it as an alternative fuel source (90). When used in sub-zero conditions, the waxy solidifications in the SME will clog filters within the fuel system. In terms of concrete, the solidified SME would clog the pores of the concrete, presumably further reducing fluid ingress.

4.5.2 Concrete Freeze-Thaw Durability

The sealants performance for preventing damage from freeze-thaw was tested using ASTM C666 (91). Samples were prepared from mixture M45. The samples were demolded after 24hs and sealed in double plastic bags for 60d. After this time the samples were opened and allowed to dry at 23℃ and 50%RH for 10d. At this time sealants were applied. The SME-PS was applied by submerging the samples in the sealant for 6h (Dose 1) and 24h (Dose 2). The solvent based silane was applied in an even coating with a paint brush. Prior to starting testing, sealants were allowed to cure for 7d and then samples were submerged in saturated lime water for 48h. The relative elastic modulus can be seen in Figure 4.7 and change in mass can be seen in Figure 4.8.

The use of the solvent based silane sealant slowed the effects of freeze-thaw damage. Prior to 100 cycles, samples treated with the SBS received 50% less damage than untreated samples. After 100 cycles both the SBS treated and untreated samples were at the same level of damage. After 75 cycles the cover of the untreated and SBS began to spall. The loss of concrete can be seen in the dramatic loss of mass seen in Figure 4.8 and Figure 4.9. The use of SME-PS sealant dramatically reduced the damage from freezing and thawing. The samples with the smaller dose of SME-PS showed no damage until 75 cycles and the larger dose showed no damage until 150 cycles. Even once damage started it was significantly less than the untreated samples. Upon completion of the testing (300 cycles) the untreated and SBS treated samples had a relative modulus of approximately 55%. This is below the failure threshold defined by ASTM C666 of 60% (91). Both of the SME-PS treated samples received less damage, maintaining approximately 85% relative modulus at the conclusion of the test (300 cycles).

4.5.3 Sealant Freeze-Thaw Durability

When concrete samples treated with the solvent based silane sealant were tested for water absorption, the amount of water absorb by these samples was reduced by approximately 95% as compared to untreated samples (87). When testing for resistance to freeze-thaw durability (91), samples treated with this sealant did not show the same reduction in water absorption.

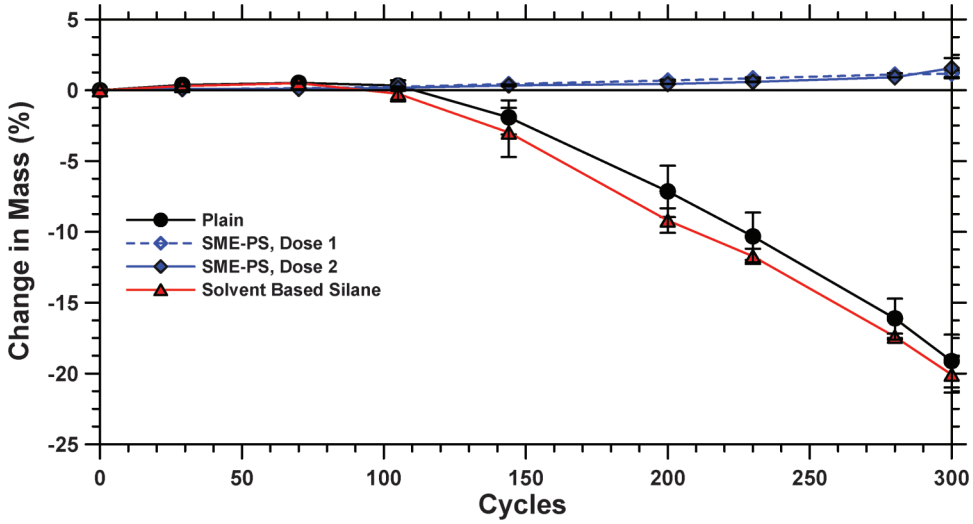


Figure 4.8 Freeze-Thaw Experimental Results, Mass Change

The silane sealants used in this study are not 100% active ingredients. The silane was transported by an inactive carrier. The silane in SBS was dissolved in isopropanol. The WBS was an emulsion of silane and water. As the sealants cures the carrier fluid evaporates and leaves behind the silane forming a protective membrane on the concrete. As the membrane is exposed to freezing temperatures it is susceptible to thermal contraction. If the forces become large enough, the membrane could begin to crack and loss effectiveness. Unlike the silane sealants, the SME never "cures" or hardens. When SME is applied to concrete, it is absorbed into the pores and remains fluid. Any thermal contraction would not result in the development of tensile stresses in the sealant.

In order to test this hypothesis, mixture C40 was treated with the sealants and tested for water absorption using ASTM C1585-04 after being exposed to freezing and thawing cycles. Samples were conditioned at 23℃ and 50% RH for 12 months prior to the application of the sealants. The sealants were applied in the same manner as described in the water absorption. Prior to testing, the samples labeled "Freeze" were exposed to 7 freezing-thawing cycles between 5℃ and −18℃. After 3 days of testing these samples are exposed to a daily freezing cycle (without being removed from the water). The efficiency of the sealants, reduction in water absorption compared to untreated samples, can be seen in Figure **4.10**.

Figure 4.9 Freeze-Thaw Samples after 280 cycles. Untreated (Plain) Samples and SBS Treated Samples Show Significant Cover Loss. SME-PS Treated Samples Show No Visual Damage

From Figure **4.10**, there was only slight differences (up to 5%) between the absorption behavior of the samples that underwent freezing and those that were kept at 23℃ within the first three days of testing. From this it can be implied that none of the sealants tested were vulnerable to freeze-thaw damage when the concrete was dry. After three days of testing, samples were exposed to daily freeze-thaw cycles (12 hours at −18℃ and 12 hours at 5℃) while in water. Following the additional 7 freeze-thaw cycles all of the sealants tested lost some of their efficiency. The most vulnerable sealant type was the SBS, which absorbed 85% of the volume of water absorbed by untreated samples following freezing. The least vulnerable sealant was the SME-PS. It only lost about 20% efficiency after freezing and thawing. Please note that the WBS only lost 23% of its effectiveness during this testing. It is believed that the emulsifying agents left in the concrete allowed for some movement of silane as the concrete was being damaged. This will lead initial effectiveness of the sealant under these conditions, but this effect will eventually wear out. This is indicated by the slope of the freezing/thawing WBS being steeper than that of the freezing/thawing SME-PS. It is likely that the WBS would continue losing effectiveness quicker as this test continued.

4.6 Chloride Ingress

When water migrates into concrete, it often times does not travel alone. Typically the water will bring dissolved solids and ions into the pore system with it. One of the most detrimental substances brought along

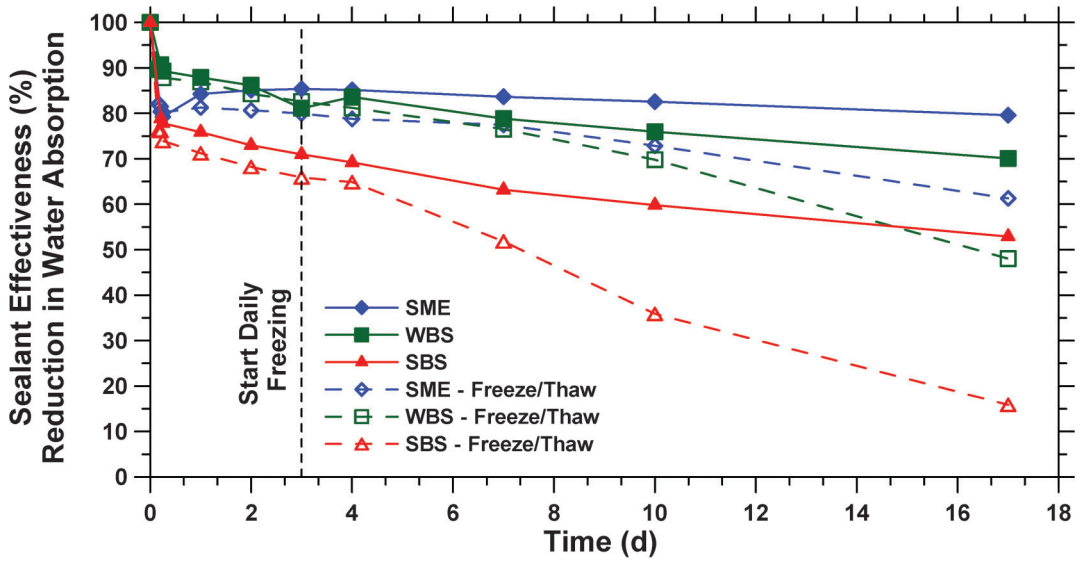


Figure 4.10 Sealant Effectiveness after Freezing and Thawing

with the water are chloride ions. Chlorides have the special ability to dramatically accelerate the corrosion rate of embedded reinforcing steel. As the steel corrodes a twofold attack is underway against the concrete. As the steel oxidizes, it loses the tensile strength in which it was intended to provide to system. In addition, the volume of the resulting oxide layer is greater than that of the initial steel. This increase in volume induces tensile stresses into the concrete which lead to the development of cracks and scaling.

4.6.1 Chloride Ingress Experimental Results

To test the ingress of chloride ions into concrete, saw-cut joint specimens of mixture M42 were created. These specimens, as seen in Figure **4.11**, were 10 cm × 10 cm × 10 cm mortar cubes. On the top face of this cube a 2.5 cm × 2.5 cm well was cast in place. 24 hour after casting, the specimens were demolded and a 1" deep saw cut was cut into the middle of the well. At this time the specimens were sealed for 14 days and then allowed to dry in a 50% RH chamber for an additional 90 days. The sides of the specimen were dammed with epoxy to form a reservoir to hold the salt solutions. This specimen geometry was selected as it attempts to mimic the behavior of a saw cut joint in the field (86).

After the construction of the epoxy damns, the samples were treated with the topical sealants. The sealants being tested are SME-PS (2 dosages), Solvent Based Silane, and Water Based Silane. For SME-PS dose 1, SBS, and WBS the sealant was pooled in the reservoir for 6h. For SME-PS dose 2, the sealant was pooled for 24h. The sealants were allowed to cure for 7d prior to the addition of the salt solutions.

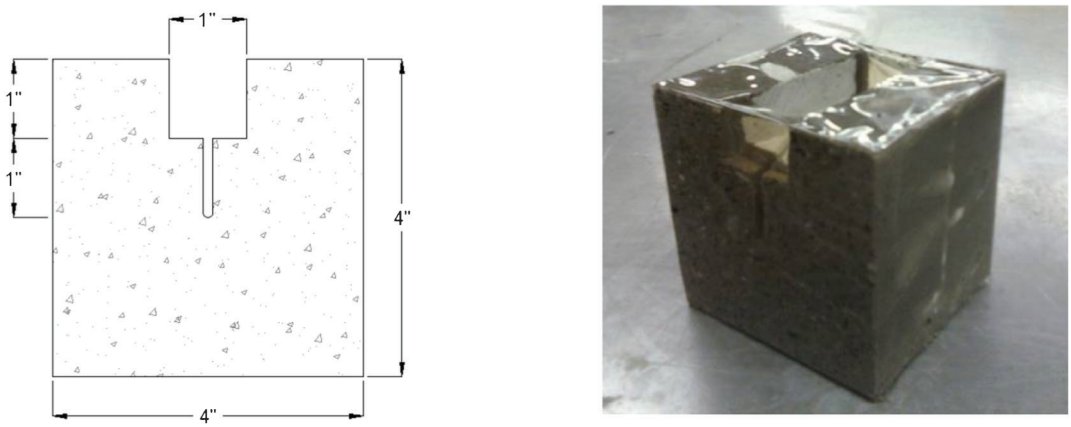


Figure 4.11 Chloride Ingress Specimen a) specimen geometry, b) epoxy reservoir

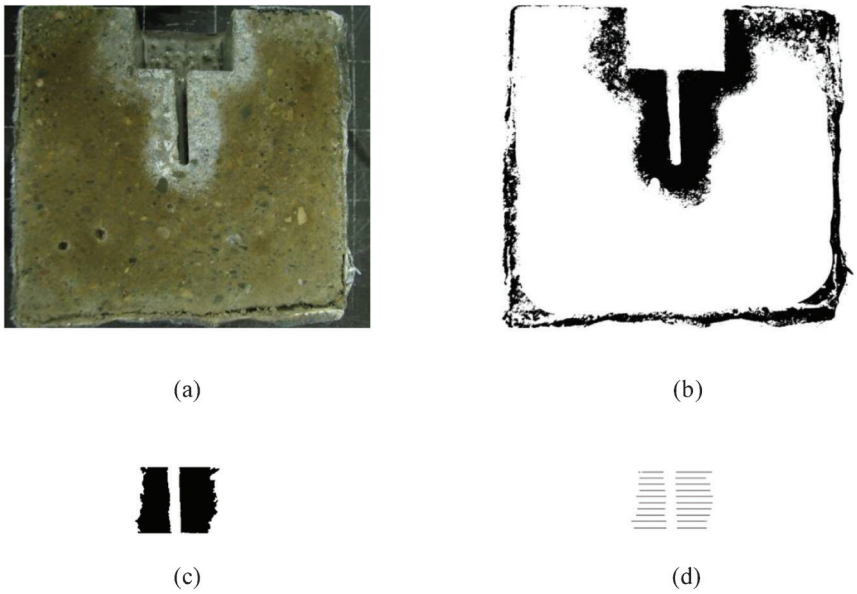


Figure 4.12 Chloride Ingress Image Analysis. (a) typical chloride Ingress sample, (b) binary image of chloride Ingress, (c) up close of chloride Ingress, (d) linear approximation of chloride ingress

For this series of tests three salt solutions were used. The three solutions are all commercially available de-icing solutions of 23% Sodium chloride (NaCl), 30% Magnesium chloride ($MgCl_2$), and 32% Calcium chloride ($CaCl_2$). These are commonly used solutions because they supply the eutectic concentrations of these salts, providing a solution with the lowest melting point. These salts solutions were pooled in the reservoir for 21d and 42d. At this time the samples were saw cut and 0.1M Silver nitrate ($AgNO_3$) was applied to samples. A white precipitate (AgCl) forms on the sample in the presence of chloride ions. This reaction will occur when the chloride ion concentration is over 165 ppm (92). These samples were photographed and the images were analyzed to determine the chloride penetration depth.

In order to determine the penetration depth of chlorides, image analysis software known as Image J was utilized. The analysis started with the color image of the salt ingress. The image was reduced to a binary image using the color of the salt as a threshold value (Figure 4.12b). After the obtaining the binary image, the file was clipped in order to focus on the region of chloride ingress (Figure 4.12c). A grid with 2mm spacing was then laid on top of the ingress in order to measure the penetration depths at these points (Figure 4.12d). The ingress measurements were imported into a spreadsheet where they could be average. The depth of chloride ingress for this experiment can be seen in Figure 4.13.

The SBS sealant was the most effective of the sealants at reducing chloride ingress. This sealant completely eliminated any ingress of chlorides for the $MgCl_2$ and $CaCl_2$ solutions and reduced the penetration depth by 80% at 42d for the NaCl solution. When using SME-PS, the dosage rate of sealant was directly related to its effectiveness. The samples were treated with a larger dosage of SME-PS resulted in a reduction of chloride depth about 10% greater than that of the smaller dosage. The least effective sealant for preventing chloride ingress was the WBS. After 42d of ponding, the chloride penetration depth was reduced by 35%, 10%, and 0% for the NaCl, $MgCl_2$ and $CaCl_2$ solutions respectively.

4.7 Conclusions

This chapter reported results of experiments to evaluate the use of Soy Methyl Ester Polystyrene (SME-PS) as a topical concrete sealant to increase the durability of concrete pavement joints.

The penetration depth of SME-PS is dependent on concrete moisture level, size of PS molecules, and time. As the concrete moisture level increases, the amount of SME-PS absorbed will decrease. As the chain length of PS increases, the amount of SME-PS absorbed will decrease. Initially SME-PS penetrates concrete quickly however over time this rate slows. Experimental results show that the greater the penetration depth of SME-PS, the more effective it is at increasing concrete durability.

SME-PS dramatically reduced damage from freezing and thawing. After 300 cycles, the untreated samples had a relative elastic modulus of 55% compared to the 85% of the SME-PS treated samples.

In general, the use of SME-PS blends as a topical sealant was successful. Samples treated with SME-PS were more durable than untreated samples. As the dosage rate of SME-PS increased, the samples had a higher resistance to deterioration.

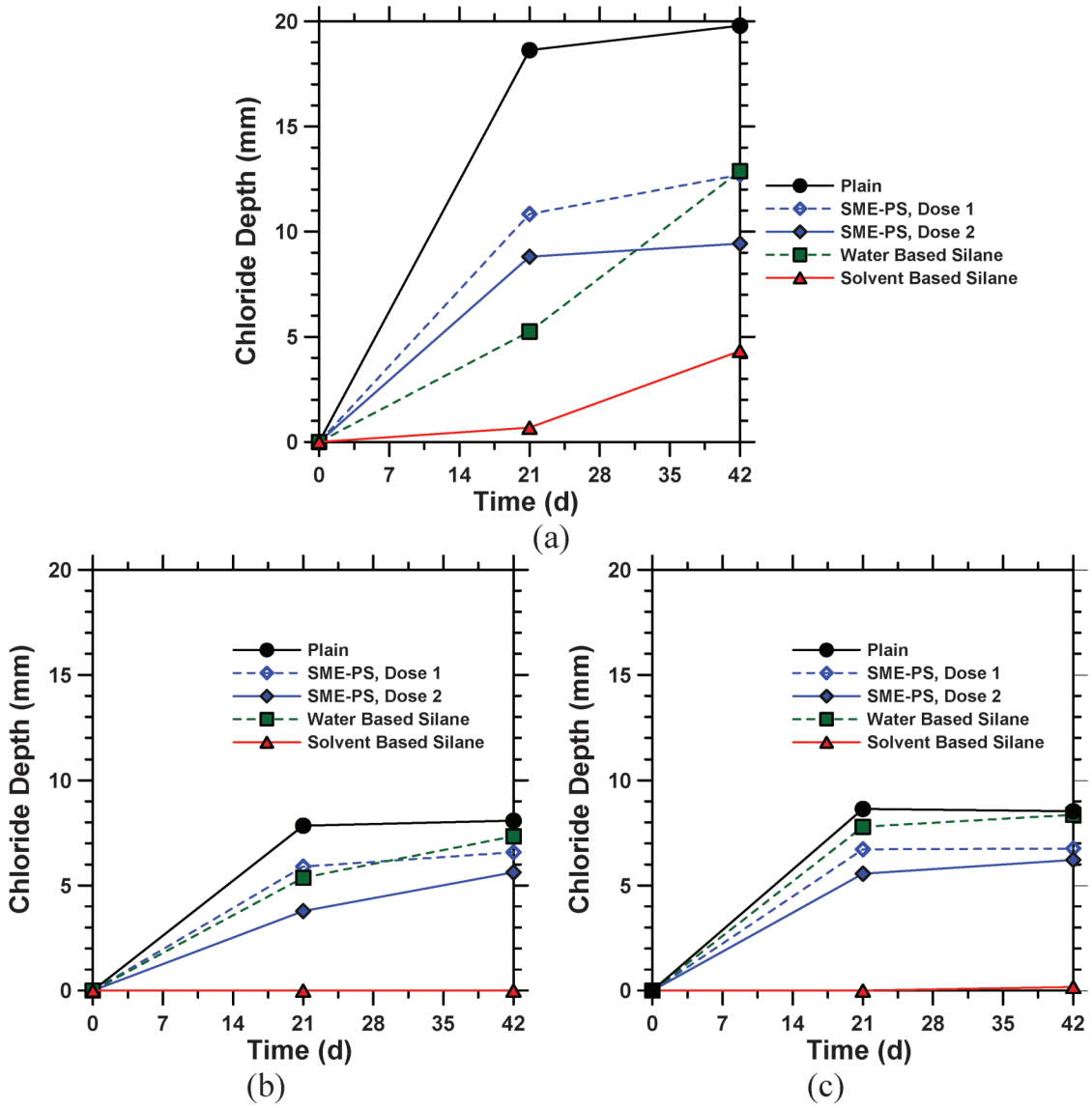


Figure 4.13 Chloride Ingress Depth (a) sodium chloride, (b) magnesium chloride, c) calcium chloride

CHAPTER 5: SUMMARY AND RECOMMENDATIONS

5.1 Background and Hypothesis

The objective of this project was to determine a plausible cause for the premature deterioration at concrete pavement joints. This project originated with the concept that the fluid (water with deicing salts) that sits in the longitudinal joint of concrete pavements can lead to preferential saturation. This concept was developed in 2005 when the principal investigator observed standing fluid in the longitudinal joints of I-65 during an series of investigations with R. Newell. During these investigations it was observed that standing water and damaged pavement joint sealant were present at each location where premature damage of the longitudinal joint was observed. This pattern of standing water (fluid) and sealant damage was noticed in subsequent field visits where low spots in pavements, or sections that retained water were the most likely to have joint damage. Premature damage was also observed in transverse joints that had appeared to not crack.

It was hypothesized that water (fluid) standing in the joint may lead to water saturation that can lead to freeze thaw damage or chemical attack. It was reasoned that by reducing the standing water (or fluid) in the joint, the potential for joint saturation can be reduced. By reducing the potential for saturation, it was reasoned that the pavement joint would be more durable over time.

It was also noted by the PI that the pavement joint sealant originally designed to keep fluid out was keeping water in since it was preventing the drying

effects associated with traffic. Each of the aforementioned factors can lead to the pavement joint holding fluid. This could lead to the pavement joint becoming preferentially saturated leading to freeze-thaw damage at the joints.

There are other factors that can contribute to joint deterioration however. It has been discussed (Nantung personal communication) that changes in tie bars have occurred resulting in a higher stress transfer and smaller crack opening. It has also been discussed by Olek (SPR 3016) that changes in the air void system (volume or spacing) or infilling of the air entrained voids may be the cause of joint deterioration. It has also been suggested by some that deicing salts (super salts) are the cause of this joint damage. A review of potential damage mechanisms is being performed by Whiting and Olek (SPR 3506).

This report is intended to compliment the ongoing study of field investigations performed by Olek (SPR 3016) where damage at the joints of PCC pavements is being investigated. Further this compliments investigations on the role of anti icing chemicals on pavements (SPR 3091) by investigating the potential for specific mechanisms to occur. This work in this report has focused on fluid ingress, the relationship between a critical degree of saturation and freeze-thaw damage. This work also evaluates a potential method to reduce fluid ingress with a sealant that penetrates concrete.

The hypothesis of this report, "standing fluid in concrete pavement joints leads to preferential saturation and once a critical saturation is reached freeze-thaw damage can occur" appears to be plausible based on the research presented in this report. In light of the plausibility of this hypothesis it is recommended that INDOT should begin to examine how changes in design and maintenance can be used to reduce the potential for preferential joint saturation. It is recommended that the joint be made free of standing water or deicing solution whenever possible. It should be noted, as mentioned earlier, that some members of the SAC have also noticed damage in pavements at other locations which may or may not be attributed to the mechanism discussed in this report. Further it has been mentioned that some cores in joints appear cracked and the joints still show distress. It is plausible that another source of distress is causing this damage or it is plausible that the crack has not opened sufficiently, or healed/locked such that water cannot drain. If the crack permits the drainage of water it would be unlikely that standing water would occur and permit preferential saturation.

5.2 Summary of Research Findings

A three-fold approach was taken in the research. This project began by examining the similarities and differences between drying and wetting of concrete in the presence of water and fluid solutions containing deicing salts. This research then related the rate of fluid absorption to a degree of saturation as a function of time. It is proposed that concrete will exhibit freeze-thaw deterioration once a critical degree of saturation is reached (in this case 86 to 88%). The time that it takes the concrete to reach a critical degree of saturation was used to describe the freeze-thaw resistance of the concrete. Concrete sealants were then suggested as a potential method to reduce potential for a concrete to absorb water and saturate, thereby increasing the resistance to freeze-thaw damage. The following section provides greater background and details on the findings.

First, the project evaluated the similarities and differences between drying and wetting of water and solutions containing deicing salts (Chapter 2). It was observed that the rate of fluid absorption (sorptivity) was related to the square root of the ratio of surface tension and viscosity. This is an important finding since deicing solutions tend to increase surface tension in a relatively linear fashion by a small amount (less than 20 to 30%). The viscosity is much more non-linear with an increase in salt concentration. This increase in concentration also increases viscosity much more substantially (up to 8 times). As a result, deicing solutions are absorbed in concrete more slowly than pure water (to an absorption rate that is as low as 30% of the rate of water absorption). This was the case whether the deicing material was the fluid being absorbed or if water was absorbed into a concrete that had previously been exposed to deicing salt solutions. This was observed for both $MgCl_2$, $CaCl_2$ and to a lesser extent NaCl.

Further it was observed that the deicing solutions have an equilibrium relative humidity that is lower than that of water. This implies that concrete containing deicing salt solutions will not dry until the relative humidity of the environment is lower than the equilibrium relative humidity (this is approximate). This was observed for both $MgCl_2$, $CaCl_2$ and to a lesser extent NaCl. The implication of this observation is that concrete containing deicing salt solutions will dry out more slowly and to a lesser extent than concrete that contains deicing salt solution. As a result it is expected that concrete that has been drying and wetting in the presence of deicing salts will be more saturated than concrete exposed only to drying and wetting with water. This may have profound implications on the time it takes to reach the critical degree of saturation under drying and wetting conditions. As such further study is needed to understand the drying and wetting behavior and its relation to saturation in field conditions.

Second, the project evaluated the role of fluid absorption rate and degree of saturation on how the concrete will behave when exposed to freezing and thawing. It is suggested that concrete will exhibit freeze-thaw deterioration once a critical degree of saturation is reached, irrespective of whether the concrete contains air entrainment or not. Air entrainment was found to reduce the degree of saturation initially and to extend the time it takes to reach a critical level of saturation. Acoustic emission was used to detect the onset of freeze-thaw damage and was used to determine the

severity of damage. It was observed that once the concrete reaches a critical level of saturation that freeze-thaw damage is imminent and stiffness degradation occurs very rapidly.

Third, the project evaluated the potential role of penetrating concrete sealers in reducing fluid transport at or near saw-cuts in pavements. Specifically a penetrating concrete sealer made using soy methyl esters was found to reduce water absorption at room temperature but also during the process of freezing and thawing. ASTM C666 tests performed using the soy methyl ester had a substantial improvement in durability as can be seen from visual evidence and as measured by stiffness degradation.

In addition, the project also examined the role of curing at the joints. It was suggested that the curing compound could be washed away during saw cutting and a second layer of curing compound may need to be applied after the saw cut was placed. While poor curing can lead to a concrete with a more open pore network it is currently though that the application of a soy-based sealer would have more benefits than applying a second layer of curing compound.

The aforementioned discussion should not be thought of having eliminated the potential salt crystallization pressures, air void filling, chemical degradation, or another mechanism as contributing to joint deterioration. It simply suggests that water ingress and saturation is a key mechanism.

5.3 Recommendations for INDOT

This research project examined the potential mechanisms that could be associated with preferential saturation at the joint due to standing fluid. It was suggested that when deicing salt solutions are present in the concrete joint it is less likely to dry and it is believed that this may lead to more rapid saturation at the joint. It was also shown that while air entrainment substantially lengthened the time it took for critical saturation and freeze thaw damage to occur, it did not prevent freeze-thaw damage. Further it showed that slight increases in air were not substantially changing the time for saturation. As such the hypothesis that standing fluid is a potential contributing cause for joint deterioration appears to be substantiated. If this is the case INDOT should begin to examine how changes in design and maintenance can be used to reduce the potential for preferential joint saturation.

It is proposed that INDOT consider the possibility of altering pavement joint design by considering a single pavement cut and sealing the concrete (using a penetrating sealer) rather than the process of sealing the pavement joint. It should be noted however that this recommendation is based on the desire to keep the water out of the concrete and a separate analysis would be needed on whether the subgrade can effectively accommodate the increased fluid that may come through the joint. The assessment of increased water on the performance of the drainable subbase is currently being conducted on other INDOT projects. Further, the potential for incompressible materials working their way into the joint would need to be considered. While this may not solve the problem of water ponding in the joint it can protect the concrete from absorption and it would allow traffic to help remove water from the joints.

It is recommended that INDOT begin to evaluate the degree of saturation for variety of concrete paving mixtures. This would require the adoption of a test similar to ASTM C1585 however an improved preconditioning period would be needed. This recommendation from an improved preconditioning procedure comes as a result of SPR 3093 that showed the current standard fails to achieve equilibrium. Further SPR 3093 showed that the degree of saturation is strongly influenced by the water to cement ratio of the mixture as well as the presence of air entrainment. It would be expected that this would also be influenced by the presence of supplementary materials like fly ash or slag. The degree of saturation testing could be done during the mixture qualification procedure and could provide INDOT with an index that involves a simple measure that may describe a concrete's durability.

It is also recommended based on SPR 3093 and previous work that a rapid measure of electrical conductivity/resistivity be investigated for potential implementation as a quality control procedure. While not a perfect test, the electrical conductivity or resistivity test is sensitive to changes in water concrete/porosity. This can shift the emphasis from strength and thickness to a platform that also includes properties that are related to durability. A current implementation plan has been requested by INDOT for the use of electrical conductivity and the PI is drafting that proposal.

It is noted that follow up projects are being conducted to determine 1) whether joint damage can be detected early using ground penetrating radar or some other non-destructive technique, and 2) how soy methyl ester sealants work as a potential for improving pavement joint performance in the field. These would need to be completed before a final recommendation on joint design/maintenance could be issued.

5.4 Recommendations for Further Study

There are several areas that require further research. They are outlined below. It should be noted that while this list makes several recommendations it is not intended to be inclusive.

- The time it takes to reach the critical degree of saturation under drying and wetting conditions is influenced by the salt concentration. As such, further study is needed to understand the drying and wetting behavior for pavements in the state of Indiana. This would require relating the sorption/desorption behavior described in Chapter 2 with weather data from the state of Indiana. Preliminary work at Purdue has shown promise in doing this; however the model would require further work.

- It is being observed by Olek et al. (SPR 3016) that some pore filling takes place in the entrained air voids. This also supports the observations of this study that high levels of water saturation are present in the concrete since this would require some fluid to be present in the air entrainment. The criteria require for freidel salt or ettringite formation is based on the chemistry of the cement and potential supplementary materials being used. It would be helpful for a model to be developed that quantifies the amount of pore filling that takes place over time as this will also increase the rate at which concrete reaches a critical degree of saturation since the pore filling appears to reduce the total space available.
- A procedure is needed to assess the life cycle performance of concrete that contains penetrating sealers and a maintenance plan needs to be developed. Chapter 4 for example presented evidence on how penetrating sealers reduce water ingress and how this can improve freeze-thaw resistance. It is currently not known however how long these sealers will remain effective or what reapplication rate should be used. Scientific quantification of this is needed.
- Additional studies are needed to better understand the interaction between the quality of the air void system and the critical degree of saturation that is needed to initiate freeze thaw damage. Specifically this work investigated three air conditions based on total volume. Additional work would be beneficial in relating the quality of the air void system with the critical level of saturation, rate of absorption, and freeze-thaw behavior.
- The majority of research to date has been performed using saw cut joints. INDOT has recently discussed the use of finished surfaces coming from 'plowed' joints. An investigation of the difference between a plowed joint and a saw cut joint should be made.
- Information is needed to better understand how different salts interact with the concrete matricies and the aggregates in the concrete. For example, it appears plausible that a time scale can be applied to a variety of degradation mechanisms. A listing of all potential deleterious reactions should be listed and examined with regard to feasibility and time scale in future work.
- It appears the physical properties of the salts may be able to be altered to reduce their potential interaction with the concrete pavement. This could make the salts more effective by keeping them at the surface of the pavement during weather events.
- Information is needed about the concentrations of salts that may be expected in the pavements at various times of the year.
- A more comprehensive approach to durability is needed where material properties can be determined from tests and where these material properties can be used directly to compute deterioration and failure mechanisms.

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