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Deicer-Freeze-Thaw Resistance Characteristics of Portland Cement Concrete for Wisconsin Pavements

Final Report

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Final Report
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For

WISCONSIN DEPARTMENT OF TRANSPORTATION
Division of Highways
Bureau of Highway Engineering, Office of Construction
Pavement Research and Performance
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Deicer-Freeze-Thaw Resistance Characteristics of Portland Cement Concrete for Wisconsin Pavements

Abstract

This study was initiated to identify Portland cement concrete (PCC) mixes that offer increased deicer-freeze-thaw durability and to identify mix characteristics that may contribute to premature durability distress. The occurrence of PCC pavement durability problems in Wisconsin and potentially related concrete durability problems in other parts of the United States are briefly reviewed as background to this study. PCC mixes covering a range of air contents and water-cement ratios were mixed in the Wisconsin Dept. of Transportation (WisDOT) Central Office laboratories and evaluated at the University of Wisconsin-Madison. Evaluation included measurement of dimensional change, weight loss and dynamic modulus of elasticity during a regime of accelerated freeze-thaw cycling in a sodium chloride/calcium sulfate solution. Petrographic examination was conducted on specimens of each mix following the freeze-thaw testing. The study did not succeed in producing concrete specimens that mimicked the deicer distress found in certain Wisconsin pavements. The study did establish that higher cement contents and resulting low water-cement ratios offer considerable additional protection for deicer-freeze-thaw exposure and more protection than simply increasing air content alone. Lowering overall sand content appeared to also improve deicer-freeze-thaw durability compared to otherwise similar mixes and cement contents.

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1.0 Problem Statement

While the vast majority of Portland cement concrete (PCC) pavements are durable in the Wisconsin climate, some Northern Wisconsin pavements have shown premature distress probably related to deicer-freeze-thaw durability. This distress was described as "extensive and continuing distress at joints and cracks, early in the pavement's life."[1] The distress appeared as a paste deterioration problem occurring at transverse and longitudinal joints and random cracks[2]. The distress started at the top of the slab and progressed downward. Symptoms associated with this distress seemed to indicate a lack of freeze-thaw durability.

2.0 Objectives and Scope of the Study

The objectives of the study were to identify PCC mixes that offer increased deicer-freeze-thaw durability and to identify mix characteristics that contribute to premature durability distress. PCC mixes covering a range of air contents and water-cement ratios were mixed in the Wisconsin Dept. of Transportation (WisDOT) Central Office laboratories and evaluated at the University. Evaluation included measurement of dimensional change, weight loss, and dynamic modulus of elasticity during a regime of accelerated freeze-thaw cycles. Petrographic examination was conducted on specimens of each mix following the freeze-thaw testing. The project was sponsored by the WisDOT and the Wisconsin Concrete Pavement Association (WCPA) with WisDOT providing project administration and technical liaison. WCPA provided funding and technical input.

3.0 Background on the Pavement Distress Problem

Prior to and during the course of this study several investigations were conducted to explain the distress, resulting in several theories. Distressed pavements under study included:

* State Highway 17 & 70 at Eagle River
* U.S. Highway 8 - West of Tomahawk
* State Highway 13 - Prentice Bypass

Several undistressed pavements were studied to provide comparison to the concretes from the distressed projects. The only obvious common aspect of the distressed concretes was the use of coarse aggregate consisting of igneous glacial gravel. Concrete cores were taken from the distressed and undistressed pavements for petrographic analysis.

3.1 Work by American Engineering Testing, Inc.

Initially the pavement deterioration was attributed to "deicer distress." American Engineering Testing, Inc. under contract to National Minerals Corporation concluded from an investigation with laboratory concretes that pavement deterioration was the result of exposure to a deicing agent with high sulfate impurities[3]. They conducted rapid freeze-thaw testing with immersion of the specimens in a sodium sulfate solution once every 30th cycle. The combination of deicer attack and freeze-thaw exposure was considered particularly destructive. The formation of ettringite crystals was believed to eventually fracture the cement paste.

Later, under contract with the Wisconsin Dept. of Transportation, American Engineering Testing conducted a petrographic examination of cores from the distressed projects as well as cores from similar, but undistressed projects[4]. Deposits of secondary ettringite were found within air voids at various depths and to varying degrees at all locations. The distribution of ettringite increased in the voids adjacent to the joint surfaces that were distressed. Ettringite formation was present in concretes with various sources and types of coarse aggregate. Distress was not associated with alkali-silica reaction. The deterioration and cracking was related to freeze-thaw durability as the air void system became filled with ettringite.

3.2 Work by the Army Corps of Engineers

Petrographic examination of a similar set of cores from distressed and similar, undistressed projects was conducted by the Army Corps of Engineers at the request of the Wisconsin Dept. of Transportation[5]. They found a consistent level of ettringite throughout the depth of the cores, suggesting that increased sulfates did not originate from the surface application of a deicer. They concluded that the most likely cause of the distress was freeze-thaw damage resulting from an inadequate air-void system. In their view, the ettringite came after the distress rather than causing the distress. It was further clarified that some cores showed deterioration but did not have significant amounts of ettringite present.

3.3 Work by Jan Skalny on Behalf of Portland Cement Association

A third analysis of distressed cores was conducted by Consultant Jan Skalny[6]. He concluded that the distressed samples had low amounts of air and that cracking was not associated with ettringite formation. Because ettringite crystallizes by a through-solution mechanism, it was reasoned that pores and voids filled with ettringite must be filled with water and therefore ineffective in resisting freeze-thaw. Ettringite was found in many air voids. Several concrete processing issues were also raised as possible secondary causes leading to the distress.

3.4 Work by the Wisconsin Dept. of Transportation

In early 1992, the Wisconsin Dept. of Transportation Materials Science Section began a laboratory study that examined the deicer-freeze-thaw durability of 32 different mixes. Mixes were based on WisDOT Grade A-WR for no fly ash and Grade A-FA for fly ash-containing mixes. Different sources and types of fly ash and cement were used in the test mixes. The test procedure consisted of subjecting 102-mm by 102-mm by 406-mm (4-in. by 4-in. by 16-in.) prisms to ten freeze-thaw cycles each week and one drying cycle in a 60°C (140°F) oven. During the thaw cycle the prisms were subject to a sodium chloride/calcium sulfate solution. Concrete prisms were evaluated for expansion, weight loss and subsequently subject to petrographic examination. Petrographic examination revealed no significant formations of crystalline ettringite.

3.5 Related Studies and Events

During the time of this investigation, concrete deterioration with potentially related circumstances was occurring elsewhere. A large lawsuit involving the deterioration of concrete railroad ties caused considerable investigation into possibly related concrete deterioration. Both alkali-silica distress and sulfate distress associated with expansive forces of ettringite formation were investigated as causes. From this investigation further attention and investigation concerning ettringite formation occurred.

Wiss, Janney, Elstner Associates[7] cited delayed ettringite formation as a recent and recurring problem in distressed concretes they have investigated including the railroad tie case. Delayed ettringite formation has been found in concretes years after casting and exposed to large amounts of water. Although delayed ettringite formation is sometimes associated with heat treated (or steam cured) concrete the distinction with *secondary* ettringite formation is not universally accepted terminology. The exact cause of increased ettringite presence continues to be debated with one possible cause cited by Hime[7] being increased sulfate contents in cements. It was noted that air-entrained concrete will provide a relief valve to the delayed ettringite formation, but only until the air void system becomes filled and no longer viable. It was also stated that temperatures as low as 54°C to 68°C (130°F to 155°F) destroy crystallized ettringite, but the possibility exists that it will reform later and cause expansive forces. According to Hime, what initially appears to be an alkali-silica attack sometimes is actually a delayed ettringite attack.

Also, during the time of the Wisconsin pavement distress, the Iowa Department of Transportation has investigated potentially related distress problems in their concrete pavements[8]. During the mid-1980's pavement distress was noted that was initially diagnosed by a consultant as an alkali-silica attack problem. A second investigation by a consultant in 1993 provided petrographic examination of over two dozen cores and found only two of the cores to contain significant damage[9]. Damage was associated with alkali-silica reaction and lack of freeze-thaw durability associated with an inadequate air void system. Despite these findings, Iowa DOT, in their own investigations, found no causal mechanism for significant alkali-silica damage and SEM-based investigation revealed large amounts of ettringite were plugging air voids of some concretes[8]. Microscopic evidence showed cracking that emanated from filled air voids suggesting that considerable expansive pressure was generated by the ettringite formation. Further investigation by the Iowa DOT has revealed that sodium chloride appears to dissolve the ettringite back into solution until conditions are right for the ettringite to recrystallize. Iowa DOT cites eight to ten of their pavements that are showing signs of similar deterioration and believe that this delayed ettringite (or secondary ettringite) formation has become a critical durability problem.

Bonen[10] recently provided a concise primer on the chemistry of ettringite formation and provided yet another view on the possibility of delayed ettringite formation. His investigation was related to the railroad tie case mentioned above. He confirms that in a water-free environment ettringite decomposes at 50°C to 82°C (122 to 180°F) and at slightly higher temperatures in the presence of water. It was also revealed that ettringite not only appears as needle or rod-shaped crystals where space is available for crystallization but in limited spaces its form can be more nondescript. Steam curing or any high temperature condition destroys all preexisting primary ettringite. Delayed ettringite formation involves dissolution of the existing monosulfate grains, ion transport, and redeposition of ettringite in relatively large spaces and other porous and calcium hydroxide-rich zones. Bonen confirms the viewpoint that the formation of strings of ettringite will cause expansive forces and microcracking.

Day[11] provided a recent literature analysis of the effect of secondary ettringite formation on concrete durability. He found that there is little potential for secondary ettringite formation problems in North American cast-in-place concrete construction; however, in heat-treated concretes significant deterioration can occur. Secondary ettringite formation can produce destructive expansions and cracking. Exposure to considerable amounts of water is essential to secondary ettringite formation. All other factors being equal, concrete made with limestone aggregate may be less susceptible to secondary ettringite damage.

4.0 Methodology and Testing Regime

The test method mimicked that of a Wisconsin Department of Transportation in-house study (see Sect. 3.4) that was being completed in the same time period. The combined compatible results of the WisDOT study and this study were expected to provide more certain conclusions than either study conducted independently could produce. Nine different concrete mixes were designed and made to establish specimens for subsequent deicer-freeze-thaw exposure with the WisDOT A-WR mix serving as the control. Mixes were varied according to water-cement ratio, air content, and sand content. Specimens were formed for freeze-thaw testing in which the specimens were immersed in the same sodium chloride/calcium sulfate solution as used in the WisDOT investigation.

4. 1 Concrete Mixes

The concrete mixes are described and consisted of the proportions shown in Table 1. To maintain consistency with the WisDOT test program the prisms were fabricated in WisDOT Central Office Laboratories with a combined crew from WisDOT and the University. Aggregates were obtained from Lincoln County by WisDOT and consisted of igneous crushed gravel. All mixes used LaFarge Type I Alpena cement and no fly ash. Table 2 shows the basic fresh and hardened properties associated with each mix.

Table 1. Concrete mix proportions

Mix No.	Description	Cement kg/m^3	Fine Aggregate kg/m^3	No. 1 Stone kg/m^3	No. 2 Stone kg/m^3	Net Water kg/m^3
1	State A-WR mix (CONTROL)	314	887	542	542	144
2	prisms cut from State Hwy 8 (one of the distressed pavements)	301 + 44.5 Class C fly ash	43%	28.5%	28.5%	Not Available
3	7 bag, high air	392	803	491	491	144
4	7 bag, moderate air	392	803	491	491	147
5	6 bag, high air	335	854	522	522	135
6	6 bag, moderate air	335	854	522	522	135
7	5 bag, lower air	279	906	554	554	139
8	State A-WR with lower sand content	314	730	621	621	136
9	7 bag, moderate air, lower sand content	392	660	562	562	144
$1\ kg/m^3 = 1.6856\ lb/yd^3$						

4.2 Freeze-thaw Testing

Four 76-mm by 102-mm by 406-mm (3-in. by 4-in. by 16-in.) prisms were fabricated from each mix and three from each set of four were designated for freeze-thaw testing. A spare prism from each mix was held in reserve for contingencies. During the casting process brass rods were placed through two locations across the 76-mm (3-in.) dimension in the prism molds and spaced 254 mm (10 in.) apart to enable dimensional change measurements of the prisms. The Highway 8 prisms were saw cut from Highway 8 using the same dimensions and dimensional change measuring pins were drilled and epoxied into the 102-mm (4-in.) faces of the specimens. All specimens were wet cured for 28 days, allowed to air-dry for an additional 28 days, and then frozen to -18°C (0°F) until freeze-thaw testing began. Although ASTM C666 suggests a 14-day curing period, the 28 day wet plus 28 day dry regime was chosen to more closely reflect field conditions.

The test regime called for 20 freeze-thaw cycles per week using Procedure A in ASTM C666[12] followed by oven drying once per week at 60°C (140°F) to promote crystal growth as done in the associated WisDOT study. The freeze-thaw cycles took the specimens from -18°C to 4°C (0°F to 40°F) five times daily for four days per week. Freezing and thawing occurred in an aqueous solution of 5 percent sodium chloride and 1 percent calcium sulfate to simulate deicer effects, again, as used in the WisDOT study. The freeze-thaw units were calibrated using a certified thermometer and thermocouples prior to beginning testing. Once per week the specimens were weighed, dynamic modulus of elasticity was measured, length change was measured, and the specimens were photographed, all after they had cooled to room temperature following the oven drying cycle. The specimens followed a rotation plan as they were placed back in the freeze-thaw units to ensure that each specimen equally experienced any deviations in temperature that are inherent in the freeze-thaw cabinets. Specimens were subject to as many as 575 freeze-thaw cycles if distress was not severe enough to warrant prior removal from the test regime.

Table 2. Fresh and hardened properties of the mixes

Mix No.	Description	water/ cement	slump, mm (in.)	Fresh air content	Unit Wt. kg/m^3 (lbs/ft^3)	28-day Compressive Strength, GPa (psi)
1	State A-WR mix (CONTROL)	0.46	38 (1½)	4.7%	2387 (149)	32.0 (4650)
2	prisms cut from State Hwy 8 (one of the distressed pavements)	na	na	na	na	na
3	7 bag, high air	0.37	44 (1¾)	8.3%	2291 (143)	30.5 (4420)
4	7 bag, moderate air	0.38	44 (1¾)	6.8%	2339 (146)	33.3 (4840)
5	6 bag, high air	0.40	44 (1¾)	8.7%	2307 (144)	26.5 (3842)
6	6 bag, moderate air	0.40	25 (1)	7.2%	2339 (146)	30.2 (4380)
7	5 bag, lower air	0.50	32 (1¼)	5.2%	2387 (149)	30.6 (4440)
8	State A-WR with lower sand content	0.43	44 (1¾)	na	2339 (146)	26.9 (3900)
9	7 bag, moderate air, lower sand content	0.37	38 (1½)	6.7%	2339 (146)	30.8 (4470)

5.0 Test Results

Measurements reported in this section include expansion, weight loss, changes in dynamic modulus of elasticity, and petrographic results of the specimens during and after exposure to 575 freeze-thaw exposures.

5.1 Expansion

Length changes of the test prisms were measured once per week as described above. Figure 1 shows the average expansion of prisms from each mix versus freeze-thaw cycles. Mix 5 (6 bag, high air) expanded dramatically more than the other mixes. Failure can be considered to occur at approximately 0.10 percent expansion and thus Mix 5 failed between 350 and 400 freeze-thaw cycles. Mix 7 suffered extensive freeze-thaw damage after 300 cycles making it impossible after that point to reliably measure expansion and dynamic modulus. The other mixes expanded much less than Mix 5.

5.2 Weight Loss

Each prism was rinsed to remove loose surface material prior to oven drying each week. The resulting weight loss of prisms with respect to cycles of exposure is shown in Fig. 2. Mix 7 (5 bag, low air), Mix 1 (A-WR, Control) and Mix 5 (6 bag, high air) performed the worst. Although there are no rigid criteria for acceptable or failing performance in this test, we consider weight losses of more than 15 percent to be excessive.

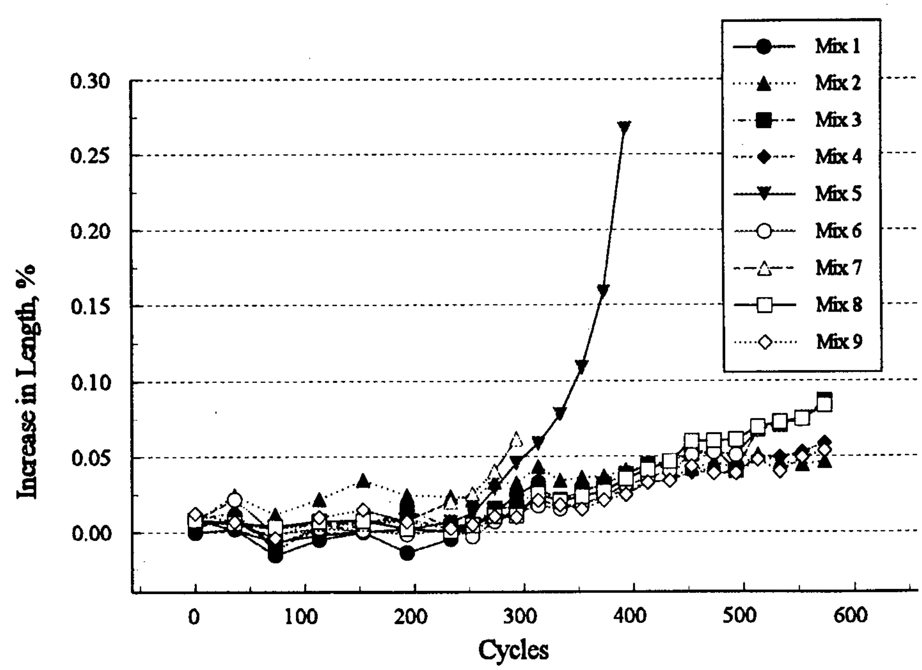

Figure 1. Increase in length for each mix with increasing freeze-thaw exposure

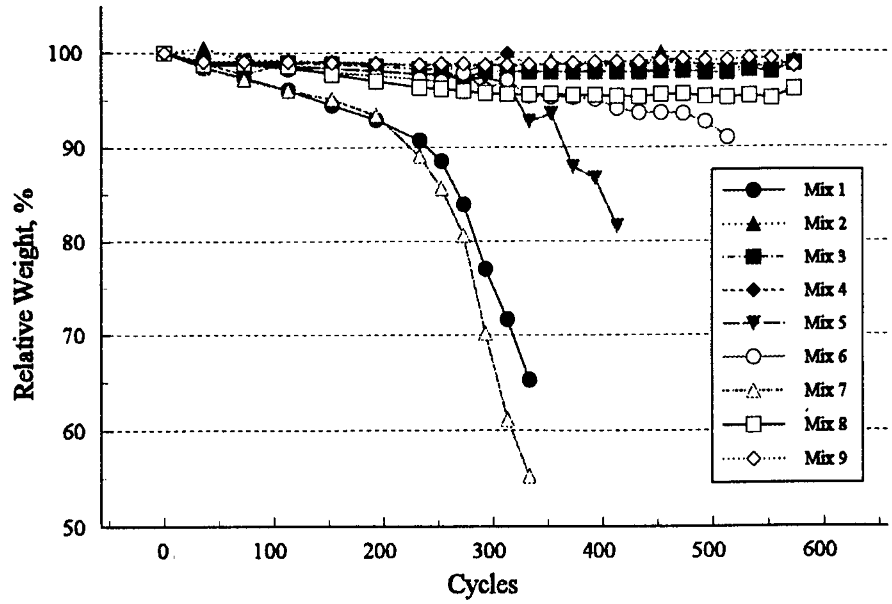

Figure 2. Relative weight loss for mixes with increasing freeze-thaw exposure

5.3 Dynamic Modulus of Elasticity

Dynamic modulus of elasticity was computed by measuring the fundamental resonant frequency of each specimen according to the forced resonant method in ASTM C 215[13]. Mix 7 (5 bag, low air), Mix 5 (6 bag, high air), and Mix 1 (A-WR, Control) performed the worst as shown in Fig. 3. Again, there are no established criteria for defining acceptable performance for this particular test using the deicer solution, but relative moduli of 75 percent or less in our opinion are showing marginal to poor durability.

5.4 Summary of Petrographic Investigation

An air void analysis and petrographic examination were conducted by W.R. Grace & Co. for the University. One specimen from the three replicates tested in the deicer-freeze-thaw regime was submitted to W. R. Grace for examination. The complete report from W. R. Grace is attached in Appendix A, but a summary is provided here.

There was no evidence of an inadequate air void system in any of the specimens. Extensive deterioration due to sulfate attack was noted with only minor evidence of freeze-thaw damage. Only Mix 2 (Highway 8) showed little or no evidence of deterioration with no loss of the original wearing surface. A summary of the air void analysis combined with measured fresh concrete air contents is provided in Table 3. ASTM C457-90 states that the spacing factor should not exceed 0.20 mm (0.008 in.) for moderate exposures and should be less for more severe freeze-thaw exposures. The highest spacing factors are noted in Mix 2 (Highway 8) and Mix 1 (A-WR, control). Mix 5 (6 bag, high air) had a high air content and very low spacing factor and yet had low durability in the deicer-freeze-thaw testing.

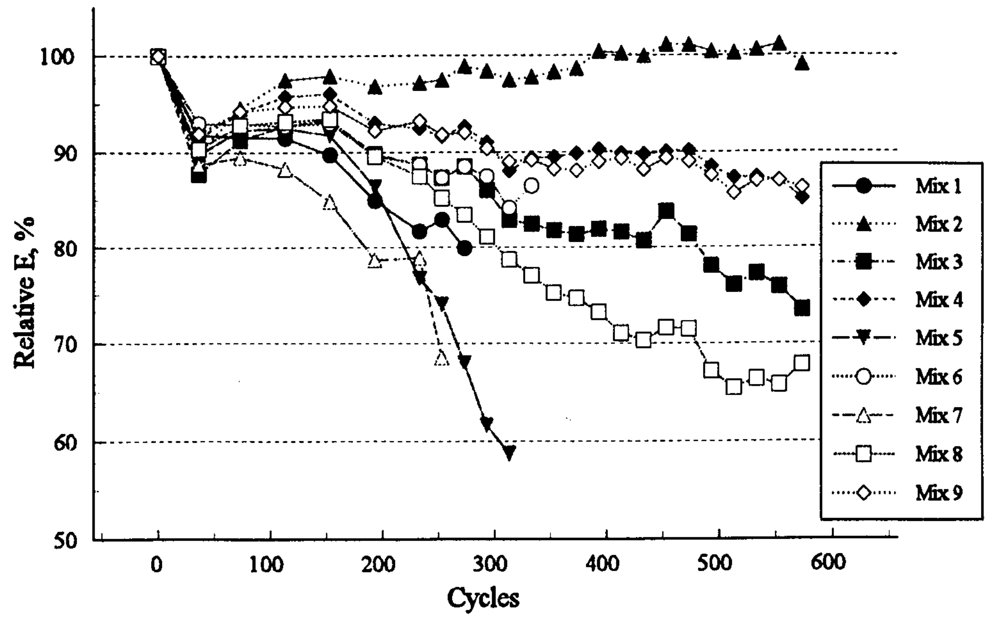

Figure 3. Relative elastic modulus for mixes with increasing freeze-thaw exposure

Subsequent x-ray diffraction of the fractured surface of the specimen from Mix 5 showed no ettringite deposits. As indicated in Table 3 ettringite deposits detected by microscopy were small or nonexistent. Hindsight suggests that the procedure of oven drying at 60°C (140°F) each week was counterproductive to generating ettringite. These temperatures were likely sufficient to destroy ettringite and occurred frequently enough to prevent large reformations of ettringite. Gypsum and calcium hydroxide were detected within the cement paste structure suggesting that the concrete was suffering from a classical sulfate attack on the cement paste.

5.5 Summary of Results

As expected, the performances of the mixes had some variation between differing measures of resistance to the deicer-freeze-thaw exposure. To provide a summary of the data, Table 4 shows the freeze-thaw performance ranking of each mix for each measurement. The rankings were totaled treating expansion, relative weight, and relative modulus of elasticity equally. For example, a mix that had the least expansion would rank ninth in expansion and with all of the other factors being equal, would be ranked first in overall favorable performance. The best performing mixes were Mix 2 (Highway 8) and Mix 9 (7 bag, moderate air, lower sand). The worst performance was from Mix 7 (5 bag lower air) although it should be noted that air void analysis showed that the air content of Mix 7 was higher than the best performing mixes. The greater age (9 years versus 56 days) of the Highway 8 prisms offered a distinct advantage over the other mixes. Cement content appeared to strongly correlate with superior deicer-freeze-thaw durability while air content did not. The effect of cement content in this study likely is associated with the decrease in water-cement ratio as cement content is increased. It is possible that similar increases in durability could be achieved by limiting water content to produce similar water-cement ratios. It is also observed in Table 4 that lowering overall sand content consistently improved durability.

6.0 Discussion

Previous investigations into a deicer distress problem in Northern Wisconsin have pointed to inadequate air void systems and/or formation of excessive amounts of secondary ettringite formation as the causal factors. In the same period, secondary ettringite formation and alkali-silica reaction have been attributed to premature distress problems in concrete pavements in Iowa and in a variety of other concrete situations. Although the symptoms of the Wisconsin distress are not identical and in many ways quite different from these other cases, the timing and similarities that do exist are reason to consider possible interrelationships.

Clearly the laboratory study reported here did not succeed in mimicking the field distress in that the causes of the distress as diagnosed by others (Sect. 3.1-3.3) were not reproduced. Secondary ettringite was not produced nor was an inadequate air void system found to be causing distress in the laboratory samples. In fact, lower air content samples outperformed higher air content samples suggesting that other factors such as lower sand content may improve durability more than small increases in air content. Higher cement content is the major factor leading to higher deicer-freeze-thaw durability. The higher cement content resulted in lower water-cement ratios. It is possible that increased durability can be achieved through water reductions rather than cement increases to yield similar water-cement ratios.

Table 3. Air void analysis results, fresh air contents, ettringite deposits

Mix No.	Description	Hardened Air Content	Fresh Air Content	Spacing factors mm (in.)	Ettringite Deposits
1	State A-WR mix (CONTROL)	5.1%	4.7%	0.20 (0.0077)	<5%
2	prisms cut from State Hwy 8 (one of the distressed pavements)	5.9%	2.5% to 5.8%	0.20 (0.008)	≈10%
3	7 bag, high air	6.7%	8.3%	0.15 (0.0058)	none observed
4	7 bag, moderate air	6.5%	6.8%	0.15 (0.0058)	none observed
5	6 bag, high air	10.0%	8.7%	0.08 (0.003)	<5%
6	6 bag, moderate air	7.0%	7.2%	0.11 (0.0045)	none observed
7	5 bag, lower air	6.8%	5.2%	0.14 (0.0057)	<5%
8	State A-WR with lower sand content	8.2%	na	0.08 (0.003)	<5%
9	7 bag, moderate air, lower sand content	5.2%	6.7%	0.17 (0.0067)	<10%

Table 4. Mix performance rankings

Mix No.	Description	w/c	Hardened Air Content	Expansion Ranking	Weight Loss Ranking	Modulus of Elasticity Ranking	Totals	Overall Rank
1	State A-WR mix (CONTROL)	0.46	5.1%	4	3	2	9	7
2	prisms cut from State Hwy 8 (one of the distressed pavements)	na	5.9%	9	9	8	26	1
3	7 bag, high air	0.37	6.7%	6	6	7	19	4
4	7 bag, moderate air	0.38	6.5%	9	8	6	23	3
5	6 bag, high air	0.40	10.0%	2	2	3	7	8
6	6 bag, moderate air	0.40	7.0%	4	4	4	12	6
7	5 bag, lower air	0.50	6.8%	1	1	1	3	9 **Worst**
8	State A-WR with low sand content	0.43	8.2%	6	4	6	16	5
9	7 bag, moderate air, lower sand content	0.37	5.2%	9	8	9	26	1 **Best**

7.0 Summary, Conclusions, Recommendations

This report summarizes the findings of a laboratory study measuring the freeze-thaw durability of Wisconsin concrete pavement mixes subject to a simulated deicer (sodium chloride/calcium sulfate solution) exposure. The major findings of this study are that higher cement contents and resulting low water-cement ratios offer more protection than simply increasing air content for deicer-freeze-thaw exposure. Lowering overall mix sand content improved deicer-freeze-thaw durability compared to otherwise similar mixes and cement contents. Increases in air content did not produce any identifiable increase in durability and may be counter-productive because of the associated reduction in concrete compressive strength. Increased air contents may be beneficial for improving durability only if it is known that air voids are being filled with deposits - a situation that did not occur to a large extent in these test specimens.

All evidence suggests that this laboratory study did not duplicate the field distress conditions as evidenced by the petrographic reports showing air void system failure and significant amounts of ettringite formations in the air voids. The petrographic examination of the specimens from this study showed little or no ettringite formation in the air void system. Coincidental concrete distress in Iowa and other cases have suggested secondary or delayed ettringite formation may be a growing problem in recent premature concrete failures. This study concludes that a modified laboratory procedure that eliminates oven drying and builds upon recent findings of the Iowa DOT will hold greater promise for producing ettringite in laboratory specimens. There is still no guarantee, however, that such a modified laboratory procedure will duplicate the field distress.

Further active investigation and continued monitoring of the national debate on secondary/delayed ettringite formation and its relationship to air void systems are recommended. This study concludes that higher cement contents and lower water-cement ratios offer a means for achieving increased deicer-freeze-thaw durability. If, despite implementation of this finding, further evidence points to secondary ettringite and inadequate air void systems as a continued source of durability distress, future testing should focus on prompting the formation of secondary ettringite in the laboratory. The effectiveness of variations in the air-void system to provide freeze-thaw durability in the presence of ettringite formation should also be examined. Test procedures used in future studies should be modified to reflect the latest information on the formation and breakdown of ettringite.

8.0 Acknowledgements

Financial support for the research and equipment in the University of Wisconsin-Madison Structures and Materials Testing Lab. provided by the Wisconsin Concrete Pavement Association and the Wisconsin Cement Shippers Promotion Fund is gratefully acknowledged. The valued technical contributions of Mr. Paul Bakke, project assistant at the University, Mr. James Parry and staff of the Wisconsin Department of Transportation and Mr. Mike Hall of the Wisconsin Concrete Pavement Association played a key role in completing the research. The contributions of W. R. Grace including those of Mr. Ed Manske and Mr. Mauro Scali in providing the petrographic analysis provided a critical element to the study and are greatly appreciated.

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Appendix A
Petrographic Report From W.R. Grace

Grace Construction Products

GRACE

CONFIDENTIAL

CONCRETE DETERIORATION
WISCONSIN DOT
9412-0380-0433
June 15, 1995

cc: Library
RFTS File
F. D. Brady
R. J. Hoopes
J. A. Kolakowski
E. F. Mansky
J. C. Murphy
K. B. Rear
C. I. Sanders
M. J. Scali
G. T. Snyder

If we don't deliver value, we haven't delivered.

CONFIDENTIAL

CONCRETE DETERIORATION
WISCONSIN DOT
9412-0380-0433
June 15, 1995

STATEMENT OF PROBLEM:

The Wisconsin DOT has set up a cooperative research program with the University of Wisconsin to determine the underlying cause(s) of distress in concrete pavements across Northern Wisconsin.

The DOT has observed the formation of secondary ettringite in the distressed concretes and several theories have been developed to explain the deterioration. However, to date, none of the theories have been proven.

The Analytical and Technical Services Laboratory was requested to conduct a series of microscopic examinations and analyses of submitted concrete samples. The laboratory study included a series of hardened air-void analyses, microscopic examinations and x-ray diffractometry. The hardened air-void analyses were conducted in accordance with ASTM C457 (linear traverse method).

SAMPLE DESCRIPTION:

The test samples consisted of nine concrete prisms, having nominal dimensions of 3" x 5" x 16" and identified as #1K - #9K. Each of the samples had been previously subjected to accelerated freeze-thaw testing, while immersed in a 5% NaCl and 1% $CaSO_4$ solution. After every 20 cycles, the samples were removed from testing and dried at 140°F, in an attempt to promote crystal growth.

RESULTS AND CONCLUSIONS:

The results of our investigation indicate that the surface deterioration is primarily due to sulfate attack, rather than cyclic freezing and thawing.

Despite the severity of the test and the obvious evidence that all of the samples have suffered some degree of distress, there is no evidence to support the theory that the deterioration is due to an "**Insufficient air-void system**". On the contrary all of the concrete samples contain air-void systems which either meet or exceed the recommended requirements for freeze-thaw durability, as outlined in the ACI 201 "***Guide to Durable Concrete***". In general, the test samples exhibit only minor evidence of freeze-thaw damage, but extensive deterioration due to sulfate attack.

Several of the test samples exhibit evidence of severe deterioration including a substantial loss of paste and aggregate. In each case, the greatest deterioration occurred on the top surfaces and sides of the test samples. In general, the least amount of deterioration occurred on the bottom surfaces of the concrete prisms. Only sample #2K showed little or no evidence of deterioration, with no loss of the original wearing surface. The other test samples exhibit a variety of distress ranging from slight surface scaling to a complete breakdown of the paste structure and loss of aggregate. A summary of the general condition and degree of deterioration observed in each sample is presented below:

Summary of Surface Deterioration

Sample ID	Extent of Surface Deterioration
1K	Severe Deterioration of Top Surface
2K	Slight to Moderate Surface Scaling on Top and Bottom Surfaces
3K	Moderate to Severe Surface Scaling, Especially on Top Surface
4K	Slight to Moderate Surface Scaling on Top and Bottom Surfaces
5K	Slight to Moderate Surface Scaling on Top and Bottom Surfaces
6K	Severe Deterioration of Top Surface
7K	Very Severe Deterioration, Especially on Top Surface
8K	Moderate to Severe Surface Scaling, Especially on Top Surface
9K	Slight to Moderate Surface Scaling on Top and Bottom Surfaces

Air-Void Analysis:

The results of the hardened air-void analyses are summarized below and presented as separate attachments to this report. The summarized data also includes a comment on the presence and estimated volume of ettringite, which was observed on the interior surfaces of individual air voids.

Air-Void Analysis Summary

Parameter	Mix 1K	Mix 2K	Mix 3K	Mix 4K	Mix 5K
Hardened Air Content (%)	5.1	5.9	6.7	6.5	10.0
Plastic Air Content (%)	4.7	2.5 - 5.8	8.3	6.8	8.7
Chord Length (in)	0.0067	0.0072	0.0057	0.0055	0.0050
Specific Surface (in)	593	557	698	722	800
Voids/Inch	8	8	12	12	20
Spacing Factor (in)	0.0077	0.0080	0.0058	0.0058	0.0030
Paste Content (%)	24.5	27	26.9	27.3	24.1
Ettringite Deposits	<5%	≅10%	None Observed	None Observed	<5%

Parameter	Mix 6K	Mix 7K	Mix 8K	Mix 9K
Hardened Air Content (%)	7.0	6.8	8.2	5.2
Plastic Air Content (%)	7.2	5.2	-- --	6.7
Chord Length (in)	0.0052	0.0068	0.0042	0.0057
Specific Surface (in)	763	589	949	700
Voids/Inch	13	10	20	9
Spacing Factor (in)	0.0045	0.0057	0.0030	0.0067
Paste Content (%)	24.1	22.8	23.5	26.9
Ettringite Deposits	None Observed	<5%	<5%	<10%

It is generally recognized by **ACI**, **PCA**, and **ASTM** that the following air void parameters are representative of a system with adequate freeze/thaw resistance:

a) **Air Content** - 6±1.5% for concretes containing 3/4" - 1" maximum sized aggregate; b) **Spacing Factor** - 0.008 inches or less; c) **Specific Surface** - a minimum of 600 square inches per cubic inch of air void volume; d) **Voids Per Inch** - a minimum of 1.5 to 2 times greater than the total % air content; e) **Average Chord Length** - sufficiently small (<0.0067 ") to insure a calculated specific surface 600 in^2/in^3 or higher and an average void spacing factor of 0.008" or less.

The **Air Content** requirement varies depending upon the maximum size of the coarse aggregate, as outline in Table 1.4.3 of the **ACI 201** ***"Guide to Durable Concrete"***.

The **Spacing Factor** is defined as the distance from any point in the paste to the edge of an air void. The value is primarily influenced by two variables; the paste content and the average chord length.

The **Average Chord Length** is based on the individually measured chord segments (edge to edge of each air void) encountered during a linear traverse of a polished sample.

The **Specific Surface** is an expression of the ratio of the surface area versus internal volume of individual air voids. It is calculated by the following equation: $\alpha = 4/\ell$, where ℓ represents the average chord length.

The data graphs used to illustrate the overall quality of the air-void systems contain two separate plots. The solid line plot represents the distribution of individual chord sizes, while the dashed line represents the fraction of the total air content made up by the individual chord sizes.

Ideally, the two graphs should nearly overlap and be as far to the left of the 0.5mm line as possible. In general, the entrapped air voids appear to the right of the 0.1 inch chord size.

It is important, when judging the overall quality of an air-void system, to look at the total air content and individual air-void parameters for void sizes **less than 1.0 mm** (center column), as well as the air-void parameters listed under the column heading "**All Voids**".

X-ray Diffraction Analysis:

The results of an x-ray diffraction analysis of sample #5K detected the presence of significant amounts of calcium hydroxide and gypsum in the paste structure. However, the presence of ettringite could not be confirmed by x-ray analysis, despite the results of a microscopic examination which clearly showed deposits of ettringite within individual air voids, as well as within the general paste structure. This apparent discrepancy can be partially explained by the detection limit (<2%) of the apparatus.

The high frequency of calcium hydroxide and gypsum are consistent with the finding that the majority of the surface deterioration is due to sulfate attack, rather than cyclic freezing and thawing. After the paste structure becomes distressed and is more open to the ingress of salt solutions, secondary deposits of calcium hydroxide and gypsum are formed in the available void spaces.

Microscopy

The results of a microscopic examination of the individual test samples are summarized below. The test results provide additional confirmation of the role of sulfate, as the primary mechanism of deterioration. The most significant findings are the overall quality of the air-void systems and the presence of ettringite deposits, within the general paste structures, as well as along the paste to aggregate bond interface of the most severely distressed concretes.

All of the paste structures exhibit a normal to advanced degree of hydration and frequent deposits of calcium hydroxide and gypsum, together with partially hydrated and unhydrated grains of cement. None of the paste structures exhibit any evidence of fly ash contamination, retarded cement hydration or lower than designed cement factors. There is no evidence of poor quality aggregates or alkali-aggregate reactivity.

Summary of Microscopy Results

Observation	#1K	#2K	#3K	#4K	#5K	#6K
Paste Color	Light to Medium Gray	Light Gray	Dark to Medium Gray	Medium Gray	Light to Medium Gray	Medium Gray
Degree of Hydration	Normal to Advanced	Normal to Advanced	Normal	Normal to Advanced	Normal	Normal to Advanced
Estimated w/c Ratio	0.45 - 0.55	0.40 - 0.50	0.35 - 0.45	0.40 - 0.50	0.40 - 0.50	0.40 - 0.50
Cement Factor	Comparable to Design	Comparable to Design	Comparable to Design	Comparable to Design	Comparable to Design	Comparable to Design
Fly Ash	None Detected	None Detected	None Detected	None Detected	None Detected	None Detected

Observation	Mix 6K	Mix 7K	Mix 8K	Mix 9K
Paste Color	Medium Gray	Light Gray	Light to Medium Gray	Dark to Medium Gray
Degree of Hydration	Normal to Advanced	Advanced	Normal to Advanced	Normal
Estimated w/c Ratio	0.40 - 0.50	0.50 - 0.60	0.45 - 0.55	0.35 - 0.45
Cement Factor	Comparable to Design	Comparable to Design	Comparable to Design	Comparable to Design
Fly Ash	None Detected	None Detected	None Detected	None Detected

SUMMARY AND RECOMMENDATIONS:

There is no evidence of inadequate air entrainment, poor aggregate quality or alkali-aggregate reaction. The results of our investigation indicate that deterioration is primarily due to sulfate attack, rather than freeze-thaw damage.

Even though some of the air-void systems contain ettringite deposits, there is no evidence that any of the air voids were filled or completely blocked by ettringite. However, the variations in the amount of ettringite suggest that the test samples may have once contained greater amounts of ettringite. It is possible that repeated heating of the test samples has resulted in a reduction in the amount of crystalline ettringite within individual air voids. In addition, a recent publication by the Iowa DOT indicates that ettringite deposits, located on the interior surfaces of distressed concretes, are soluble in NaCl solutions. After being submerged for an extended period, the ettringite deposits were no longer observed in concrete paste structures.

Any future research should include the examination of test samples not subjected to elevated temperatures. In addition, it is possible that even minor deposits of ettringite may be enough to reduce the effectiveness of air-void systems by blocking capillary pore spaces. Therefore, future investigations should also include the use of scanning electron microscopy to examine the interior surfaces of individual air voids.

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