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Reduction of Concrete Deterioration by Ettringite Using Crystal Growth Inhibition Techniques: Part II Field Evaluation of Inhibitor Effectiveness

July, 2004

Sponsored by the
Iowa Department of Transportation
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Final

REPORT

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Iowa Department of Transportation.

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IOWA STATE UNIVERSITY
OF SCIENCE AND TECHNOLOGY

Iowa Department of Transportation

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Abstract

The effects of diethylenetriaminpenta(methylenephosphonic acid) (DTPMP) a phosphonate inhibitor, on the growth of delayed ettringite have been evaluated using concrete in highway US 20 near Williams, Iowa, and the cores of six highways subject to moderate (built in 1992) or minor (built in 1997) deterioration. Application of 0.01 and 0.1 vol. % DTPMP to cores was made on a weekly or monthly basis for one year under controlled laboratory-based freeze-thaw and wet-dry conditions over a temperature range of -15° to 58°C to mimic extremes in Iowa roadway conditions. The same concentrations of phosphonate were also applied to cores left outside (roof of Science I at Iowa State University) over the same period of time. Nineteen applications of 0.1 vol % DTPMP with added deicing salt solution (~ 23 weight % NaCl) were made to US 20 during the winters of 2003 and 2004. In untreated samples, air voids, pores, and occasional cracks are lined with acicular ettringite crystals (up to 50 μm in length) whereas air voids, pores, and cracks in concrete from the westbound lane of US 20 are devoid of ettringite up to a depth of ~0.5 mm from the surface of the concrete. Ettringite is also absent in zones up to 6 mm from the surface of concrete slabs placed on the roof of Science I and cores subject to laboratory-based freeze-thaw experiments. In these zones, the relatively high concentration of DTPMP caused it to behave as a chelator. Stunted ettringite crystals 5 to 25 μm in length, occasionally coated with portlandite, form on the margins of these zones indicating that in these areas DTPMP behaved as an inhibitor due to a reduction in the concentration of phosphonate. Analyses of mixes of ettringite and DTPMP

using electrospray mass spectrometry suggests that the stunting of ettringite growth is caused by the adsorption of a Ca^{2+} ion and a water molecule to deprotonated DTPMP on the surface of the {0001} face of ettringite. It is anticipated that by using a DTPMP concentration of between 0.001 and 0.01 vol % for the extended life of a highway (i.e. >20 years), deterioration caused by the expansive growth of ettringite will be markedly reduced.

1. Introduction

During their service lives, Iowa roadways are susceptible to premature deterioration due to the growth of expansive secondary minerals in the concrete paste. These secondary minerals form years after initial highway construction and include: calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), brucite ($Mg(OH)_2$), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$). Of these minerals, delayed ettringite is probably the most abundant [1].

Delayed ettringite in Iowa highways commonly fills microscopic pores and small air voids (<100 μm in diameter) and lines the margins of large air voids (> 100μm in diameter) (Fig. 1) and occasional cracks. There is considerable controversy in the literature concerning whether cracking in cement paste is caused by the expansive growth of ettringite [1-6] or whether ettringite forms after crack development [7-11]. Regardless of its role in concrete deterioration, previous research has shown the expansive nature of delayed ettringite, but the mechanisms involving expansion remain in doubt since it is unclear whether they are topochemical in nature or due to through solution [1]. Where delayed

ettringite formation has been shown to produce damage in concrete, it is generally associated with heat cured concrete treated to temperatures > 70°C, rather than concrete cured at room temperature [12]. However, it is clear that ettringite is an expansive mineral in highways cured under normal weather conditions [1].

Sulfate is a necessary component for ettringite to form and can originate from internal or external sources. Internal sources of sulfate can originate from pyrite (FeS_2) inclusions in dolomite and limestone aggregates. The pyrite oxidizes to form goethite (FeO(OH)) or ferrihydrite ($Fe(OH)_3$) and releases sulfate [13]. External sources of sulfate include natural or polluted groundwater, sulfur dioxide from the combustion of fuel, and sulfur impurities of deicing salts applied to roadways in winter [14].

Previous research involving crystallization inhibitors show that delayed ettringite growth, concrete expansion, and damage can be reduced in controlled experimental conditions [1,15]. Cody et al. [15] evaluated the nucleation rate, growth, morphology, and stability of ettringite in the presence of more than 300 chemicals and admixtures. The plasticizers sorbitol, citrate, and tartrate were found to inhibit ettringite nucleation and growth as did certain lignosulfonate air-entrainment admixtures. Lee et al [1] evaluated the effects of four different crystallization inhibitors: two phosphonates, HEDP [1-hydroxyethylidene-1,1-diphosphonic acid] and DTPMP; a phosphate ester, NTP [nitrilo-tri(ethyl acid phosphate)]; and a polyelectrolyte, PA (polyacylic acid) on ettringite growth in highway concrete. Concrete blocks from Iowa highways as well as fabricated

and cured type I mortar (without coarse aggregate) were subjected to continuous immersion, wet/dry cycling, and freeze-thaw cycling in sodium sulfate solutions and in sodium sulfate solutions containing an inhibitor. The sodium sulfate ensured the growth of abundant ettringite crystals in the cement paste. The two phosphonate inhibitors were effective in reducing ettringite nucleation and growth in concrete, whereas the two other non-phosphonates were less effective. Of the two phosphonates, DTPMP (manufactured by Monsanto Company), was the most effective in inhibiting ettringite growth and subsequent expansion and cracking of the blocks (Fig. 2). DTPMP is nontoxic (Dequest 2060S, MSDS, Solutia, Inc.) and is not biodegradable by most bacteria. The use of DTPMP has been approved by Jim Rost, Director of IDOT Environmental Services, who considers this chemical to be environmentally safe.

Diamond [16] showed that laboratory studies of delayed ettringite growth do not always duplicate what occurs in field concretes, in large part, because the fluid composition in equilibrium with the cement paste and ettringite in each setting is often different. To follow up on the laboratory experiments and to better understand ettringite growth in field concretes, the present study focuses on the application of DTPMP to selected sections of roadway in Iowa, under normal highway weather conditions. The goal of this research is to evaluate the performance of the application of DTPMP on the prevention or reduction of delayed ettringite in Iowa highway concrete, with the main objective of preventing premature deterioration. In addition to this set of experiments, cores were obtained from selected Iowa highways and subject to periodic applications of

DTPMP at different concentrations under wet-dry, freeze-thaw and real weather conditions. It should be noted that some coarse dolomite aggregates show compositional rims (Fig. 3) that primarily result from dedolomitization reactions associated with the application of deicing salts to the highway [17].

The physical characteristics of concrete cores used in the present study are given in Table 1 and show that moderate deterioration was observed in highways built in 1992 (core identity E, F, and H) whereas only minor deterioration is present in highways constructed in 1997 (core identity O, P, and Q). Details of the core location, petrography of the aggregate, the cement mix of the core, and the proportion of sulfur-bearing minerals and oxidized products are given in Appendices A to F. Sample designations have used the following terminology. For example, sample H1 and H2 are cores 1 and 2 from location H. As samples were prepared, the cores were cut midway into two halves parallel to the surface of the core, a top and a bottom. A core from the top half of core H1 would have the designator H1T. The top and bottom of this half of the core will have the designator T (top) or B (bottom), so that a sample from the top of the top half of core from location H1 will be referred to as H1TT.

2. Experimental Design

The present study consists of four parts: 1. Application of DTPMP to test plots on the eastbound and westbound lanes of U.S. 20 near Williams, Iowa. The aim of this experiment was to determine whether or not there was any effect on the application of sodium chloride deicing salt with chemical inhibitor to

deteriorated highway (westbound) and to newly made highway that contained slag (eastbound). This was a relatively short-term project as applications were only made over two winters immediately prior to storm activity. Ideally, applications should be made and studied for a period of at least 10 years to evaluate the long-term effects of the inhibitor on ettringite growth in Iowa highways. 2. Application of DTPMP to samples of cores collected from roadways in Iowa built in 1992 and 1997. These samples were exposed to normal weather conditions as they were stored in the open on the rooftop of Science I at Iowa State University. Applications of deicing salt solution and chemical inhibitor were made on a weekly basis, regardless of weather conditions, to simulate the effects of long-term (multi-year) applications of deicing salt and chemical inhibitor. 3. Samples of core from roadways built in 1992 and 1997 were stored in a furnace and a freezer and subjected to DTPMP to mimic the extreme temperatures (-15° to 58°C) that can occur on highways in Iowa. 4. An experiment was conducted to evaluate possible chelating or inhibiting effects of DTPMP on ettringite. This experiment involved the determination of species using electrospray mass spectrometry that are produced when ettringite was added to inhibitor solution.

2.1. Field Test on U.S. 20

Two separate sections of highway were treated, one on the westbound lane of US 20 between mile markers 157.65 and 157.85 and the other on the eastbound lane between mile markers 168.80 and 169.00. Prior to the application of the inhibitor, four cores were taken from the highway approximately

120 yards from each end of both test strips. At each interval, cores were obtained from the center and edge of a panel. The westbound lane showed visible signs of deterioration with discoloration of the pavement surface particularly near panel joints. This discoloration is accompanied by fine fractures. After cutting these cores to obtain sample blocks, cracks were visible inside some of them. In other parts of the panel, the surface of the highway exhibits some pitting, scaling, and fracturing (cracks up to 0.25 inch wide). Sodium chloride brine has been applied to the highway since 1991 as an anti-icer and deicer prior to and during storms, respectively. By contrast, the eastbound section of highway was paved in 2002 and opened for traffic in November, 2003. Prior to the commencement of the study, the highway surface had not been treated with deicing salts. Slices of core were studied with a petrographic microscope and a scanning electron microscope prior to combined deicer-inhibitor applications and compared with slices of core taken from the same location at the end of the 14 month long experiments, which covered two winters (Fig. 3).

Based on data derived from the laboratory-based experiments of Lee et al. [1], 0.1 vol % DTPMP was added to deicing salt solution (~ 23 weight % NaCl) and applied to 352 yards of both test strips via a spray bar attached to the front of an IDOT truck fitted with a 22 gallon tank that would dispense inhibitor solution at a rate of 5.3 gallons per minute while the vehicle was traveling at 14 miles per hour. The pH of the solution was buffered to 10 with NaOH (~0.1 m) to approximate pH conditions of the concrete and to alleviate direct corrosion of the

alkaline cement paste with acidic DTPMP, which has a pH of <2, and to alleviate potential deleterious alkali-silicate, alkali-carbonate, and dedolomitization reactions that occur at low pH [17] (Fig. 4). Nineteen applications of solution were sprayed onto the road surface during the winters of 2003 (8 applications) and 2004 (11 applications).

2.2. Roof Experiments

Samples for these experiments were taken from cores of six Iowa roadways that were considered, on the basis of physical inspection, to exhibit minor or moderate amounts of deterioration. The physical characteristics of these cores are described in detail by Hart [18] and summarized in Table 1. For each highway location, two sets of cores were taken from the center of the panel and the right-hand driving lane near the margin of the panel. Cores were cut with a water saw into rectangular blocks that had an average volume of 72.5 cm^3 (7.4 cm x 2.8 cm x 3.5 cm). The samples were then placed on wooden pallets to raise them above the surface of the roof and subsequently divided into two groups so that chemical applications could be made on a weekly or monthly basis (Fig. 5). A total of 124 concrete samples were obtained from the 6 different roadways with 66 samples on each pallet. Tops and bottoms of core were included since they were more commonly in contact with deicing solutions on the highway compared to the center of the core.

Samples were treated with three different DTPMP-bearing solutions buffed by NaOH to a pH of 10: 0.01 vol % DTPMP and distilled water, 0.1 vol % DPTMP

and distilled water, and 0.1 vol % DTPMP with 0.75M NaCl. This combination of solution mixtures was chosen to test the effects of varying inhibitor concentration and adding saline deicing salt. Solutions were sprayed only to the top surface of the block to simulate the application of solutions to concrete surfaces in the test strips along US 20. The solutions were applied using Nalgene squirt bottles with a trigger nozzle that released ~ 1 ml of solution per squeeze of the trigger. A volume of 5 ml of solution was applied to approximate the amount of solution applied per unit area in the test strips. Solutions were sprayed on a weekly (70 applications) or monthly basis (16 applications) from the beginning of November 2002 to the end of February, 2004.

2.3. Laboratory Experiments

Wet-dry experiments and freeze-thaw experiments primarily followed the methods described in Lee et al. [1]. However, instead of completing immersing concrete blocks in solution for the duration of the experiment, the surface of concrete blocks (7.4 cm x 2.8 cm x 3.5 cm) were sprayed with the same volume of solution as that used in the roof experiments. For freeze-thaw experiments, eighteen samples were sprayed with three solutions: 0.01 vol % DTPMP and distilled water, 0.1 vol % DTPMP and distilled water, and 0.1 vol % DTPMP with 0.75M NaCl. Half of the samples were also subsequently sprayed with 5 vol % Na_2SO_4 in an attempt to induce the growth of ettringite. Both sets of samples were stored in a freezer at -15°C in individual non-reactive 250 ml Nalgene containers to ensure minimal sample contaminate. A set of three untreated

control samples were kept in other containers for comparison. Four samples were also completely submerged in 0.75M Na_2SO_4 with 0.1 vol % DTPMP and distilled water and stored in containers in a manner described by Lee et al. [1]. All laboratory experiments ran for exactly one year. Samples subjected to freeze-thaw experiments were treated with solutions on all sides of the blocks (1 ml per side) and subsequently placed in a freezer for 132 hours. Samples were then removed and air warmed to 25°C for 24 hours for a total of 56 cycles over the year long period of the experiments.

Wet-dry experiments were conducted in the same manner as the freeze-thaw experiments except that the samples were placed in a sealed furnace that was set to a temperature of 58°C (~135°F). Samples were sprayed with three solutions: 0.01 vol % DTPMP and distilled water, 0.1 vol % DTPMP and distilled water, and 0.1 vol % DTPMP with 0.75M NaCl. In addition to these solutions, half of the samples were also sprayed with a solution of 5 vol % Na_2SO_4. A total of nine samples from the six Iowa roadway cores were treated with the three solutions in addition to the sodium sulfate solution. Another twelve samples from the six Iowa roadway cores (Table 1) were treated with just the three solutions mentioned above minus the sodium sulfate solution. A set of four untreated control blanks were kept in the oven for comparison. Four additional samples were stored in 250 ml Nalgene containers and were submerged in 0.75M Na_2SO_4 with 0.1 vol % DTPMP and distilled water. Samples were treated with inhibitor solutions on all sides of the blocks (1 ml per side) and were placed in the furnace for 132 hours and then removed and air cooled to 25°C for 24 hours.

2.4. Nature of Possible Reaction between Ettringite and DTPMP

An electrospray mass spectrometer was used to try and better understand any chemical reaction that may have taken place in solution between ettringite and DTPMP. Ettringite was synthesized by dissolving $Al_2(SO_4)_3.18H_2O$ (Fisher lot 030165) in deionized water and by combining it with a saturated solution of $Ca(OH)_2$ (Fisher lot 028280) using the technique described by Cody et al. [11]. Both solutions were filtered prior to mixing and the combined solution allowed to sit at room for 24 hours whereupon ettringite was filtered from solution and allowed to air dry. 0.6 g of ettringite was subsequently combined with 250 ml of 0.1 vol % DTPMP and deionized water, with NaOH added to increase the pH to 10. First a blank solution of deionized water was run to set a baseline to eliminate background peaks. Then a solution with a concentration of 2.4 g/l of ettringite was obtained and 20 µl of this solution was diluted to 0.4 mM and introduced into a Finnigan TSQ700 electrospray mass spectrometer. To work out potential species in this solution a spectrum in negative ionization mode was obtained of a solution containing 0.1% vol DTPMP with ettringite.

3. Methods of Study

3.1 General Procedures and Instrumentation

Petrographic analyses of thin-sections were conducted with both transmitted and reflected light utilizing a standard petrographic polarizing microscope to

identify minerals and textures. Pieces of concrete core rather than polished thin sections of concrete were studied with a Hitachi S 2460 reduced-vacuum scanning electron microscope (SEM) because polishing of the thin section would likely remove or reduce soluble components. Back-scattered images obtained with the SEM were taken and energy dispersive analytical X-ray (EDAX) area maps were collected for Si, Al, K, Na, O, Ca, Mg, S, Cl, P, and Fe. EDAX point analyses were obtained at high magnification for qualitative mineral identification. An accelerating voltage of 20 kV was generally used for imaging and EDAX point analysis.

A Finnigan TSQ700 electrospray mass spectrometer was used to determine potential chemical reactions that occurred in solution between DTPMP and ettringite. The TSQ700 instrument was equipped with an API 2 interface to run in negative electrospray ionization mode. The operating voltage was set 4.5 kV with a capillary temperature of 250ºC and a sheath gas (nitrogen) pressure of 80 psi.

4. Results

4.1. Field Test on U.S. 20

Cores taken from test plots along the eastbound and westbound lanes at the end of the nineteen deicer-inhibitor applications were compared with the cores taken prior to the application of inhibitor solutions. SEM images showed that the top surface of both treated and non-treated cores contained no ettringite in air voids or large pores. This is probably due to the dynamic nature of the driving

surface of a roadway as the tire tread of a vehicle interacts with the road surface. The four cores taken from the eastbound section of U.S. 20 in this field test showed no physical, textural, or mineralogical differences to the original cores taken before the application of inhibitor solutions, except for a slight discoloration that could be seen from a cross section of the core. The discoloration (white instead of the normal blue-gray color) occurred 3 to 4 cm from the surface of the core and is a result of hydration of slag, which is an integral component of the concrete paste in the eastbound lane. Petrographic and scanning electron microscopy did not show any evidence of the presence of primary, secondary or delayed ettringite in air voids or large pores. This result is hardly surprising because the presence of slag reduces the amount of cement paste that contains sulfate and chemically reacts with calcium hydroxide so that calcium hydroxide is converted to calcium silicate hydrate instead of being converted to gypsum which can then form ettringite [19]. Moreover, this section of roadway is only 2 to 3 years old and delayed ettringite may have not had sufficient time to grow.

The field test conducted on the westbound lanes yielded completely different results than the non-reactive eastbound section. The westbound section of U.S. 20 is composed of a C-3 cement mix and is devoid of slag. SEM studies show the presence of abundant ettringite in air voids and large pores throughout the cores obtained prior to and after the deicer-inhibitor applications. SEM images show that the inhibitor solution clearly affected ettringite growth ~ 0.3 to 0.5 mm below the surface of the highway (Fig. 4). In non-treated cores (i.e. prior to inhibitor application) ettringite near the surface is ~15-20 μm in

length (Fig. 4A), with some crystals approaching ~50 μm in length, whereas ettringite crystals in treated cores were < ~10 μm in length (Fig. 4B). The middle and bottom sections of treated and non-treated cores exhibited ettringite crystals in air voids in the ~20 to 50 μm range. The morphology of crystals varied from euhedral, elongate (20 to 25 μm) crystals (Fig. 4A) to squat, irregular-shaped crystals approximately 5 to 15 μm in length. Some of these crystals are coated with portlandite (Fig. 4B) whereas others show no spatial association to portlandite but are also stunted (Figs. 4C and 4D).

4.2 Roof Experiments

The six concrete cores used for the roof experiments were C-3 and C-4 mixes (Table 1), which have an air entraining agent and a water reducer added. The water/cement ratio for these cores was 0.38 to 0.43, respectively. Transmitted light microscopy and SEM imaging of samples prior to the application of solutions containing DTPMP showed the presence of abundant ettringite in highways built in 1992 (core samples F, E, and H). Acicular ettringite crystals between ~20 and 50 μm filled air voids up to ~100 μm in diameter and generally lined the rims of air voids > ~100 μm in these samples. Ettringite was less abundant in highway concretes built in 1997 (core samples Q and P), but they still contained a significant amount of ettringite. Core sample O contained between 10 to 20 weight % fly ash and was devoid of ettringite because of the addition of fly ash to the concrete mix that gave the concrete a resistance to sulfates.

At the end of chemical applications, visual inspection of the blocks showed that they were, in general, structurally intact and devoid of cracks, pits, and scales. However, three blocks did split because of expansion due to freeze-thaw action of pre-existing cracks that were initiated during sample preparation.

We have used the term “ettringite” for the hydrated Ca-Al sulfate present in the treated highway concretes but it should be noted that another hydrated Ca-Al sulfate, monosulfate ($Ca_4Al_2SO_4(OH)_{12}.6H_2O$), will also be present when the sulfate content of the concrete paste is low. However, qualitative SEM point analyses of the hydrated Ca-Al sulfate, shown in Figure 6A, in samples F4TB, H4BB, E4TT, F1TT, and E1TM indicate that ettringite is the dominant phase. Only minor amounts of Si were detected, indicating that the thaumasite [$Ca_3Si_2(OH)_{12}.24H_2O(SO_4)_2(CO_3)_2$] component of the ettringite-thaumasite solid solution is low. Figure 6A also show the presence of a minor amount of an unidentifiable species with a very low S/Ca ratio. Yang et al. [20] also identified a similar phase in heat cured mortars.

Results showed that application of inhibitor solution at a weekly rate had a more dramatic impact on the size and abundance of ettringite in air voids and pore spaces than those subject to monthly applications. At the surface of the blocks, where the inhibitor-bearing solution was applied, SEM imaging showed there was an enormous reduction in the amount of ettringite in air voids and large pore spaces for all concrete blocks treated weekly with the same solutions used in the roof experiments (i.e., 0.01% DTPMP, 0.1% DTPMP, and 0.1% DTPMP plus 0.75M NaCl). Most air voids at or within 1 mm of the surface were devoid of

ettringite. When a solution composed of 0.1% DTPMP plus 0.75M NaCl was applied, NaCl were present in some voids and within the paste.

SEM images of samples to which DTPMP-bearing solutions were applied on a weekly basis show that phosphonate had penetrated beneath the surface of the concrete, to depths of between 1 and 6 mm. Pathways of air voids normally filled or lined with ettringite were either absent or lined with stunted or corroded ettringite crystals (Fig. 7). Below these depths, all voids and large pores were filled or lined with ettringite similar in morphology to that in untreated samples.

By contrast, for samples treated with DTPMP-bearing solution on a monthly basis some air voids at or adjacent to the surface were lined with ettringite. The presence of ettringite was confirmed by qualitative SEM EDAX analysis. Directly below the surface and throughout the rest of the blocks, ettringite was present in voids and large pores.

4.3 Laboratory Experiments

Wet-dry and freeze-thaw experiments were applied to the same six cores that were used in the roof experiments. In both sets of laboratory experiments, inhibitor solutions were applied on a weekly basis to all sides (1 ml per side) of the concrete block instead of just one side as was the case for the experiments carried out on the roof of Science I. Blocks were cut below the top surface of the core, just above the base of the core, and from the middle of the core. For both wet-dry and freeze-thaw experiments involving inhibitor-bearing solutions, SEM imaging showed that air voids at the surface of these blocks were devoid of

ettringite. Control blocks that had no inhibitor solutions applied to them exhibited no physical changes due to freeze-thaw conditions alone.

Concrete samples subject to freeze-thaw experiments at the end of one year were structurally intact, although there was scaling on the surface of sample Q3TB, with deterioration of cement paste around the margins of aggregate particles (Fig. 8). Samples immersed in 0.75M Na_2SO_4 and 0.1 vol % DTPMP exhibited scaling along the aggregate-cement paste interface whereas cracks up to 1 cm in length also occurred near the corners of blocks. Samples immersed in 0.75M Na_2SO_4 with 0.1 vol % DTPMP contained abundant ettringite throughout the blocks, and were clearly unaffected by the DTPMP presumably due to the disproportionately high concentration of Na_2SO_4. Similarly, samples sprayed with 0.1 vol % DTPMP and 5 vol. % Na_2SO_4 were also unaffected by the presence of the inhibitor. However, for these samples, Na_2SO_4 crystals grew in spaces adjacent to aggregate particles during the thaw period when samples were exposed to air for 24 hours. For samples sprayed with 0.01 vol % DTPMP and distilled water, 0.1 vol % DTPMP and distilled water, and 0.1 vol % DTPMP and distilled water with 0.75M NaCl, SEM images combined with EDAX point analysis showed the presence of corroded and stunted ettringite crystals in air voids ~1-6 mm from the surface of the block. Such crystal morphologies mimic those that formed during the roof experiments. Figure 6B shows that SEM point compositions of the hydrated Ca-Al sulfate crystals in samples P5TB, P6TB, Q3TB, H2Tb, and H4TB were primarily of ettringite with a minor amount of monosulfate. These compositions are similar to those reported for the roof

experiments. In sample Q3BT, minor amounts of alite (Ca_3SiO_5) and belite (Ca_2SiO_4), as indicated by SEM point analyses, occur as minute grains along the walls of some air voids (Fig. 9). Rather than forming as a product of the ettringite-consuming reaction, alite and belite are natural products found in Portland cement and were likely present in the walls of the void. However, where DTPMP-bearing (Na_2SO_4-free) solutions were applied, ettringite crystals diminished in size to 10 to 15μm within one month (Fig. 10). In samples, treated with 0.1 vol. % DTPMP and 0.75 M. NaCl, the random distribution of NaCl crystals throughout the concrete paste was relatively common. Although this appeared to have no major effect on the degree of deterioration of the concrete, the spatial distribution of these crystals clearly demonstrates that the infiltration of the NaCl brine was considerable. In sample P5TB, for example, an almost continuous zone of NaCl crystals from one end of the block to the other shows that the solution penetrated a minimum of 3.6 cm. There was no evidence that this zone was spatially related to fractures in the sample suggesting that the solution primarily permeated through the sample along connected pores.

Samples Q2BT, H2BT, E2BT, which were submerged in 0.75M Na_2SO_4 and subjected to wet-dry experiments, deteriorated rapidly within 3 to 4 months. Cracks developed near the corners of blocks and along aggregate-cement paste interfaces. With time, the volume and grain-size of ettringite increased and formed in both air voids and the cement paste. After ~3-4 months the volume of ettringite and associated cracks were so abundant that concrete blocks exhibited catastrophic failure and crumbled.

By contrast, the remainder of the samples that were treated with the same solutions as the freeze-thaw experiments on the roof of Science I remained structurally intact with no visible evidence for scaling or deterioration for the first five months. However, after that time, cracks began to develop throughout the concrete block with the block eventually collapsing. The concrete deteriorated due to the dehydration of ettringite and other hydrous phases in the cement paste, including monosulfate, at high temperature (58°C)

4.4 Nature of Possible Reaction between Ettringite and DTPMP

An electrospray mass spectrum was obtained in negative ion mode of a solution containing 0.1% vol DTPMP mixed with ettringite (Fig. 11). Inspection of Figure 11 shows the presence of a deprotonated DTPMP peak (molecular weight of 572.2) plus two other prominent peaks at 628.1 and 670.2. Although we are unable to identify the peak at 670.2, that at 628.1 is deprotonated DTPMP with a Ca^{2+} ion and a water molecule adsorbed onto the phosphonate ion.

5. Discussion

Deterioration of concrete in, for example, highways, heat-treated precast concrete, concrete railroad ties, and dam galleries that is caused by the expansive growth of ettringite has been supported by several studies [1-6]. Various theories have been put forward to explain ettringite-related expansion mechanisms. For example, Cohen [21] and Diamond [22] proposed that expansion was caused by crystal growth pressures whereas Mehta [23], Mehta

and Wu [24], and Mehta and Wang [25] suggested that concrete expansion is, in part, caused by water adsorption on the negatively charged surfaces of ettringite. Despite these suggestions, details of the expansive mechanism remain in question. Moreover, there is considerable debate whether ettringite is an expansive mineral or whether it simply grows in pores and cracks after their development [10-11]

Ettringite in Iowa highways occurs in air-entrainment voids, interstitial pore spaces, cracks, and along the interface between aggregate particles and cement paste and is considered by Lee et al. [2] to have been an expansive mineral that resulted in the deterioration of the highway concrete. Lee et al. [2] speculated that ettringite was precipitated directly from pore solutions in the highway concrete and that the expansive pressures developed because of ettringite growth that completely fills microscopic pores and by pressures caused by water expansion on the negatively charged surfaces of ettringite. Whether expansion is enhanced by the ice development in infilled and near-filled air voids during freeze-thaw remains uncertain, however, it should be noted that such air voids are common in the highways used in this study.

Ideally, for the highway to maintain its structural integrity, the concentration of the DTPMP inhibitor applied to the highway should be low enough to cause a reduction in the size of ettringite so that expansive pressures produced by ettringite growth on the cement paste are non-existent. However, in order to determine whether DTPMP would react with ettringite under highway conditions (rather than in the laboratory where conditions are controlled) in a

short period of time (i.e. 15 months); we chose DTPMP concentrations of 0.1 and 0.01 vol %, which we consider to be high. The results obtained from the applications of DTPMP to the westbound lane of US 20, concrete slabs exposed on the roof of Science I, and laboratory based wet-dry experiments are consistent with the phosphonate mostly acting as a chelator rather than an inhibitor, since ettringite was completely removed in some parts of the highway slab. Both the 0.1 and 0.01 vol % phosphonate-bearing solution permeated into the concrete slab and completely dissolved ettringite up to 6 mm from the concrete surface (most commonly 1-4 mm). The phosphonate-bearing solution undoubtedly migrated along microcracks, enlarged pore spaces, air voids, and distorted transition zones between aggregate and cement paste. These experiments show two important aspects: 1. The chelating solution serves to act as a tracer to the extent to which phosphonate-bearing solutions can penetrate concrete slabs over a 12-15 month period (i.e. up to 6 mm); and 2. The relative importance of chelation and inhibition of DTPMP on ettringite growth. While the process of chelation completely dissolves the ettringite, the effects of inhibition are seen at the margins of the zone of chelation where ettringite crystals become corroded and stunted. This zone presumably represents a volume where the concentration of DTPMP becomes markedly reduced to the extent that it behaves like an inhibitor. It should be stressed here that other components of the solution (e.g., NaCl) likely penetrated samples on the order of the centimeter scale. We suspect that the large size of the phosphonate molecule, the likely high adsorption rate of DTPMP, and the clogging of pores by NaCl, likely results

in localized differences in the amount of penetration of the phosphonate. The smaller NaCl molecules are less reactive with the cement paste than the phosphonate allowing it to penetrate distances on the centimeter scale.

Our understanding of the mechanism which causes DTPMP to act as an inhibitor is, in part, derived from the findings of Tomson et al. [26] who evaluated the adsorption and desorption isotherms of four phosphonates, including Dequest® 2000, Dequest® 2010, and Dequest® 2060 on calcite over a wide range of solution conditions, which included variable NaCl concentrations. The effectiveness of phosphonates as a retarder of ettringite growth was also demonstrated by Coveney et al. [26], using designed phosphonate molecules with shapes varying from linear to cyclic. In Tomson et al.'s [26] experiments, the phosphonate solution species that forms is one that essentially has Na and Ca attached to the surface of the phosphonate. The phosphonate molecules designed by Coveney et al [27] produced a marked reduction in the length of ettringite crystals.

Experiments conducted in the present study of solutions that contain DTPMP and ettringite, using electrospray mass spectrometry in negative ion mode, show the presence of an ion with a molecular weight of 628.1, which corresponds to a deprotonated DTPMP molecule with adsorbed Ca^{2+} and water. In this experiment, it is likely that the Ca ion was cleaved off ettringite and that the ion with the molecular weight of 628.1 was adsorbed onto the {0001} face of ettringite. However, in highway concretes, there are several Ca-bearing minerals in the cement paste that could also serve as the source of Ca in such an ion. In

this regard, it should be noted here that SEM imaging studies showed no corrosion along aggregate-cement paste interfaces suggesting that the breakdown and subsequent contribution of Ca from minerals in the cement paste is less likely than ettringite. Regardless of the source of Ca, such adsorption produced the stunted ettringite crystals in concrete derived from the westbound lane of US 20, slabs exposed on the roof of Science I, and in core from laboratory based wet-dry experiments.

6. Summary and Conclusion

The results obtained in this and companion studies [1,2] on the role of ettringite in concrete deterioration should have considerable implications on the way maintenance personnel treat highways over their service life. Ideally, testing of the effects of inhibitors on the growth of ettringite should be conducted on highways over a multi-year span (i.e. > 10 years). In this way, the nature and extent of ettringite growth can be evaluated as well as the amount, the concentration, and the nature of inhibitors can be tested in a realistic fashion. The present study attempts to simulate these long-term tests by conducting experiments involving a phosphonate inhibitor, DTPMP, on an operating highway (US 20), and cores from operating highways that have been subject to moderate and minor amounts of deterioration over a year long period when exposed to normal weather conditions in Iowa. We used phosphonate concentrations of 0.01 and 0.1 vol%, which are high for normal inhibitor concentrations, but it was unclear at the beginning of the experiments whether any inhibition of ettringite

growth would be observed at low concentrations. In addition, we have extended the laboratory controlled freeze-thaw and wet-dry experiments of Lee at al. [1] by exclusively testing the potential inhibition effects of ettringite growth by DTPMP, over a range of temperatures that better mimic the extremes in Iowa weather conditions. The results of all experiments in the present study have relied on petrographic analysis and SEM imaging of concrete slabs before and after year long phosphonate application. The experiments show that high concentrations of DTPMP (i.e., 0.01 and 0.1 vol. %) will dissolve ettringite in air voids, pores, and cracks up 6 mm from the surface of the concrete after only one year of phosphonate application. Note that the zone of chelation along the westbound lane of US 20 is only 0.3 to 0.5 mm deep but this is due to the fact that only nineteen phosphonate applications were made during the project. The results of highway, roof and laboratory experiments effectively show the rate at which inhibitor solutions penetrate cured concrete paste. However, the experiments more importantly show that the phosphonate acts as an inhibitor around the zones of chelation. This suggests that if concentrations of <0.01 vol % phosphonate, for example 0.001 vol%, were applied to the highway over its service life, secondary or delayed ettringite is likely to be stunted in length and will not create deterioration as a result of expansive growth. We saw no visual affect of cracking or deterioration due to reaction of DTPMP with the cement paste. The reason for the stunted growth of ettringite when treated by DTPMP is caused by the adsorption of a Ca^{2+} ion and a water molecule to deprotonated DTPMP on the surface of the {0001} face of ettringite.

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Table 1
Characteristics of Iowa highway concrete cores used in roof, furnace, and freezer experiments

Core ID	Year Built	Deterioration	Roadway	County	Mix Type	Cement	Fine Aggregate	Coarse Aggregate	Air Entraining Agent	Water Reducer
E	1992	Moderate	I-80	Iowa	C-3	Buffalo IA (I)	Disterhoff (A48508)	Sully (A50002)	Sika AER	Sika Plastocrete 161
F	1992	Moderate	SH-150	Buchanan	C-3	Mason City IA (LH I)	Hoffman (A10510)	Hazleton (A10010)	Protex AES	Protex PDA25-DP
H	1992	Moderate	SH-163	Polk/ Jasper	C-4	Mason City IA (LH I)	Colfax (A50502)	Sully (A50002)	Dara-Vair R	WRDA-82
O	1997	Minor	US-151	Linn	C-3 *(Slag)*	Mason City IA (HNIS)	Ivanhoe (A57520)	Bowser-Springville (A57008)	Daravair 1000	Sika Plastocrete 161
P	1997	Minor	SH-163	Mahaska	C-3	Louisville NE (I/II)	New Harvey (A63512)	Sully (A50002	Sika AEA-15	Sika Plastocrete 161
Q	1997	Minor	SH-137	Mahaska	C-3	Mason City IA (HNIS)	New Harvey (A63512)	Sully (A50002	Conchem Air	None

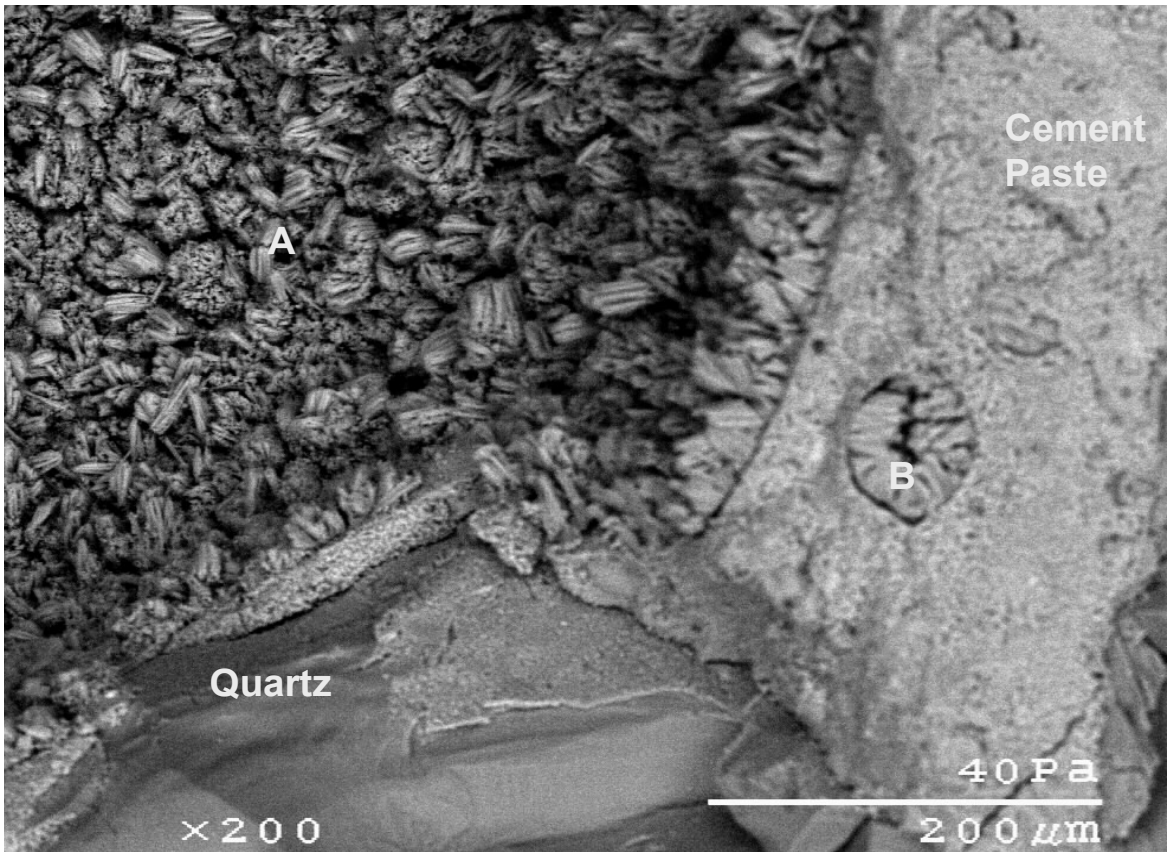

Figure 1. SEM micrograph of large (A) and small (B) air voids lined with well-formed, euhderal ettringite crystals, approximately 20 µm in length in sample "H" treated with sodium sulfate solution

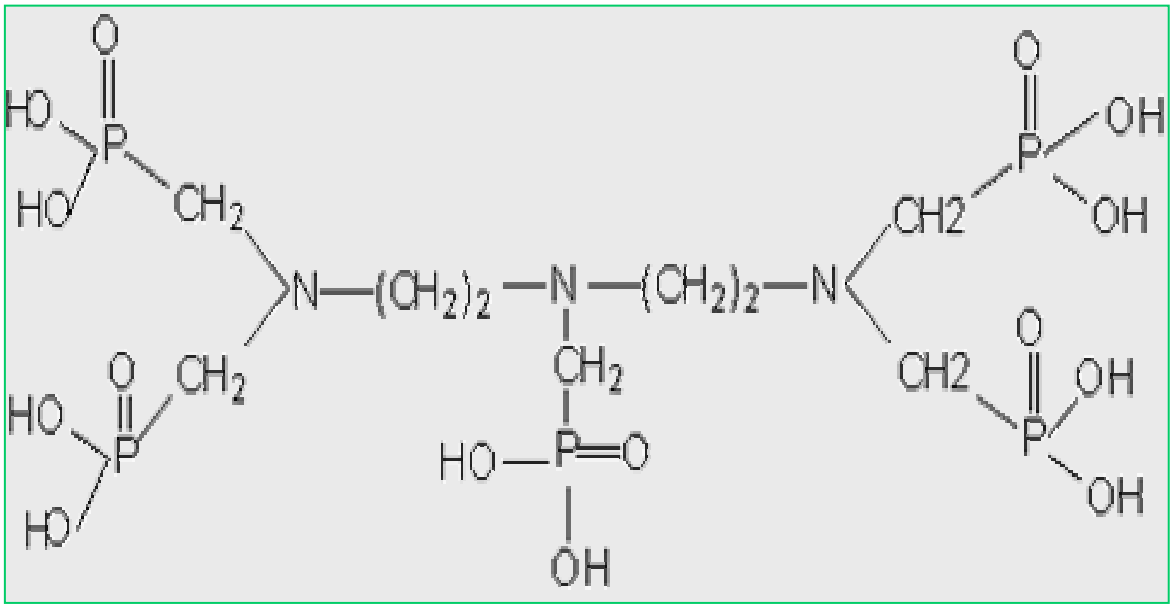

Figure 2. Illustration of Dequest 2060S (DTPMP) molecule - Diethylenetriamine penta (methylene phosphonic acid).

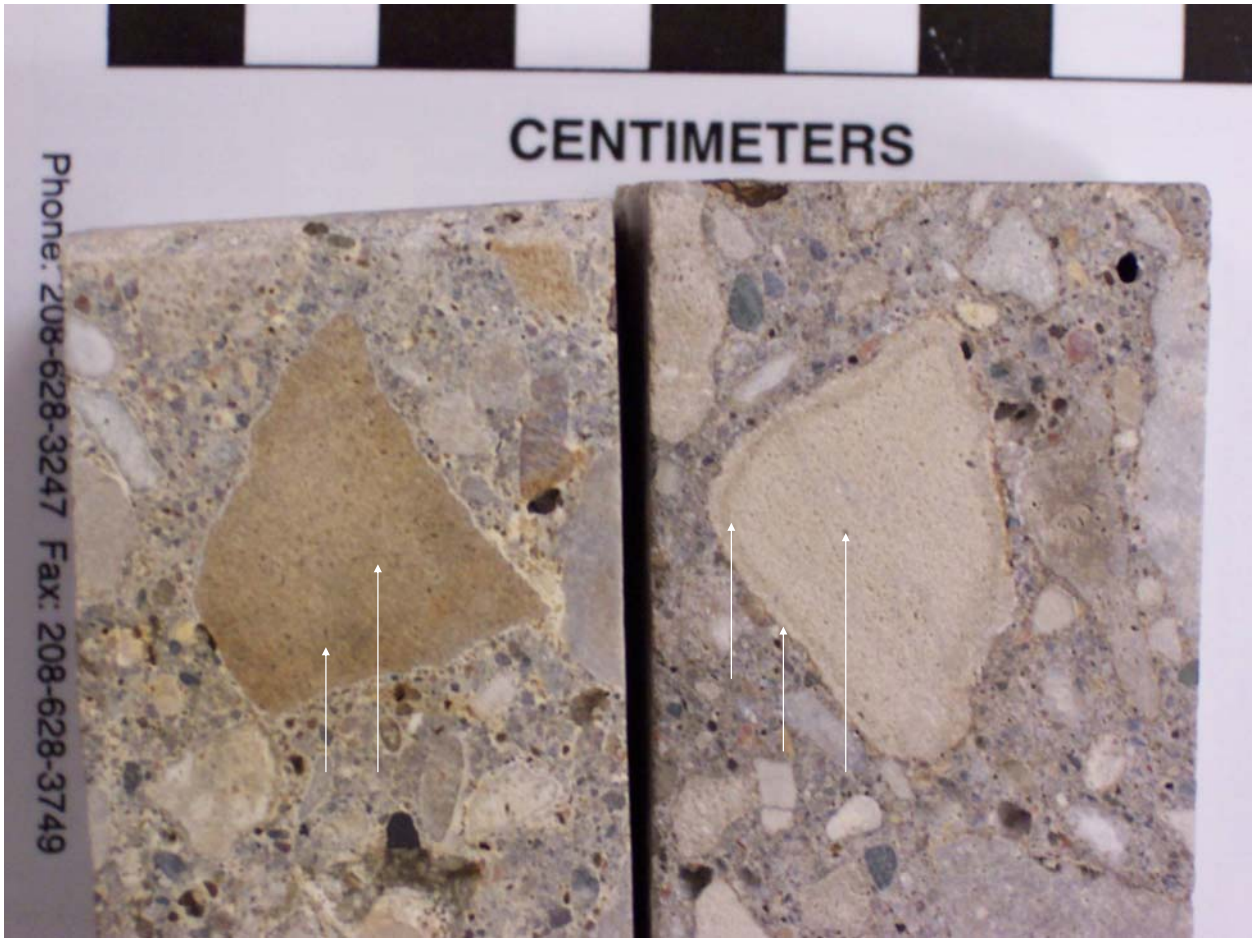

Figure 3. Concrete samples O5BB (left) and P3TB (right) showing compositional rims on dolomite particles that formed by dedolomitization reactions associated with the application of NaCl deicing salts.

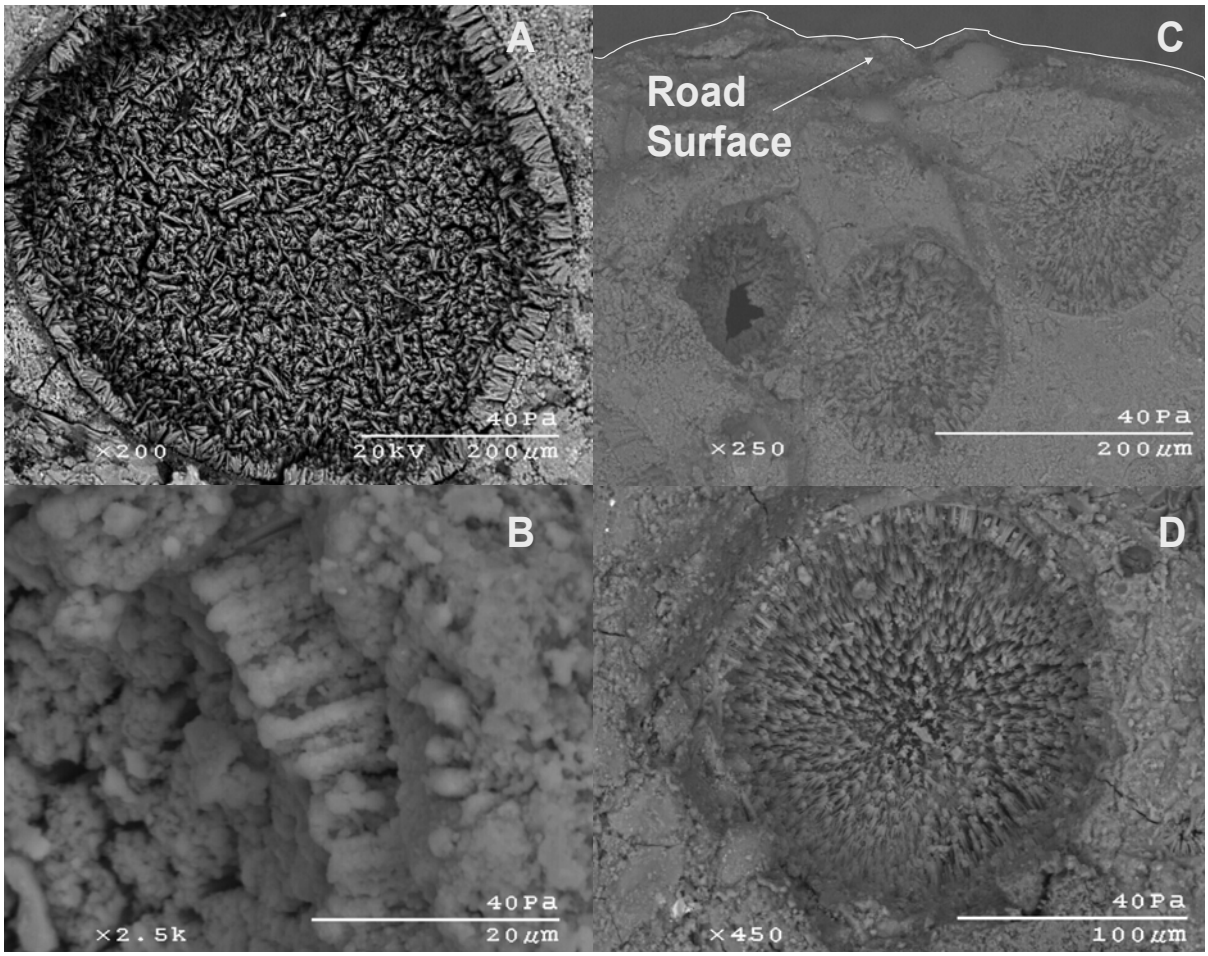

Figure 4. SEM micrographs of treated core samples from the westbound lane of U.S. 20 near Williams, Iowa. A. Ettringite crystals from core sample (E1TB) prior to treatment with inhibitor solution. B. Treated sample of core #1 U.S. 20 westbound, showing very short crystals, 0.23 mm directly below the road surface, coated with portlandite (these crystals are only ~10µm and less in length). C. Profile of treated sample of core #4 U.S. 20 westbound, showing air voids 0.33 mm below road surface. Ettringite crystals are ~20 µm in length but exhibit a different morphology than is normally seen for ettringite. D. Closeup of treated sample of core #2 U.S. 20 westbound, showing unusual morphology.

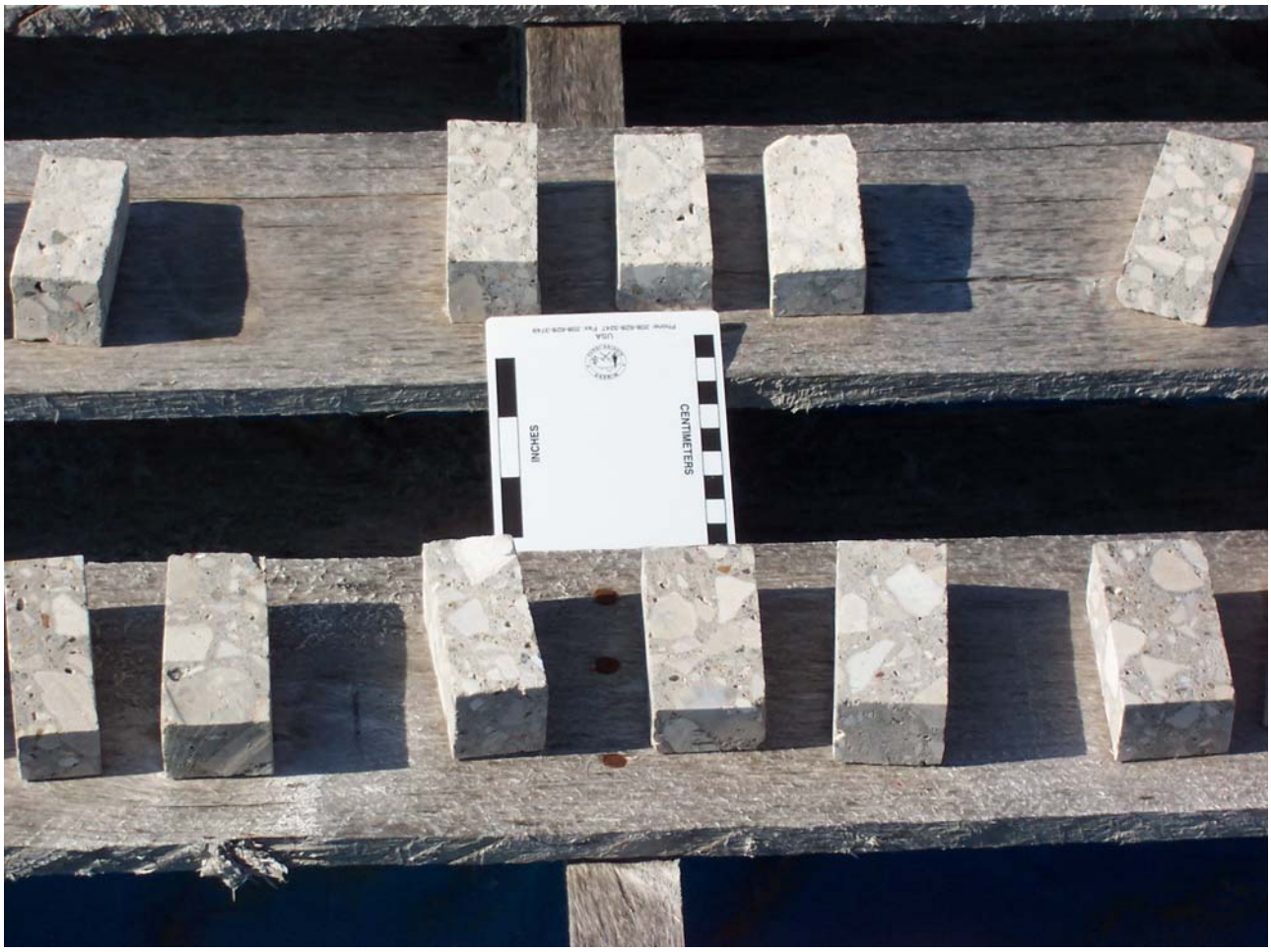

Figure 5. Layout of highway concrete samples on the roof of Science I at Iowa State University.

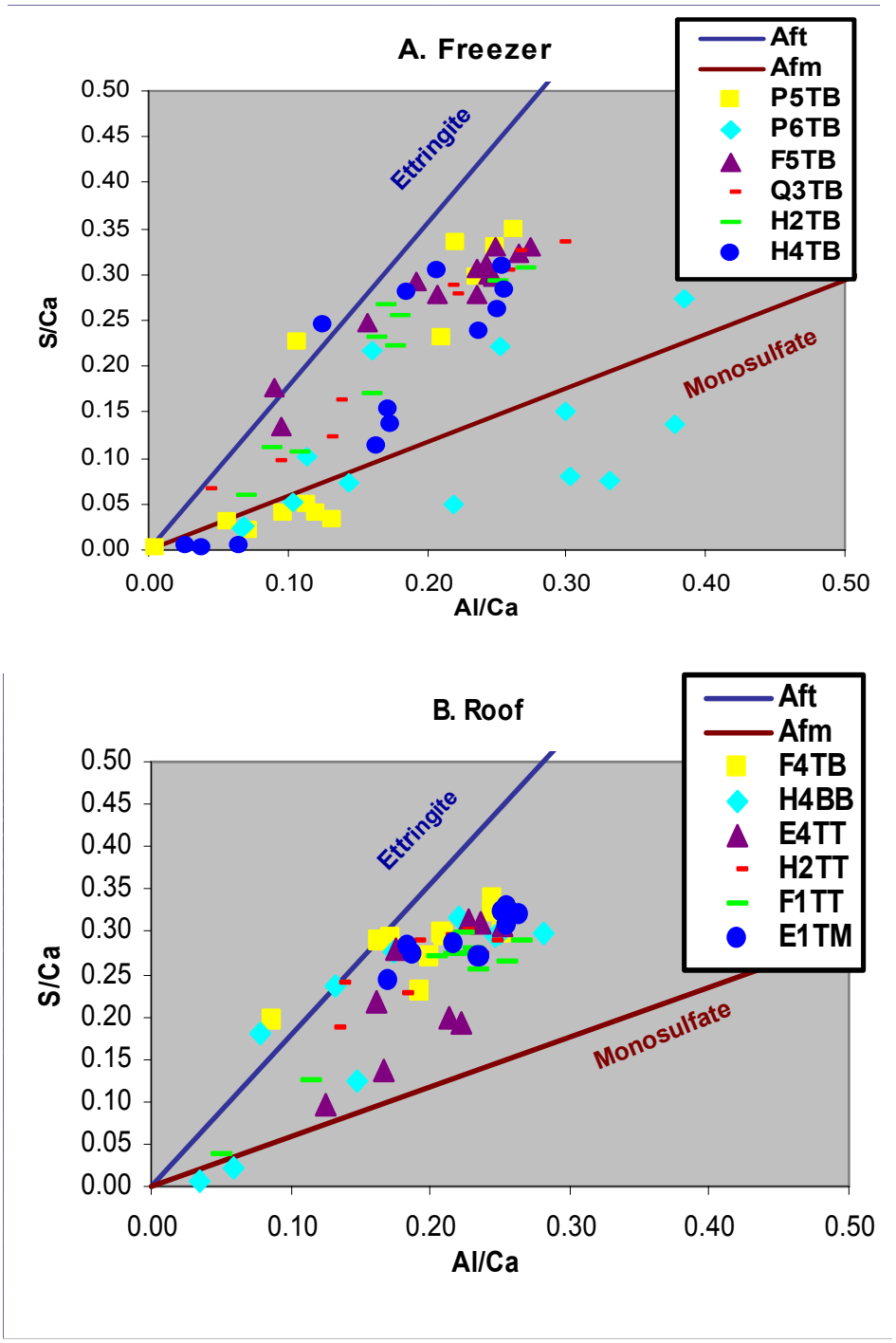

Figure 6. Atomic ratio plots of S/Ca vs. Al/Ca of hydrated Ca-Al sulfate in concrete samples from: A. Experiments conducted on the roof of Science I at Iowa State University; and B. Controlled freeze-thaw experiments. Note that for both sets of experiments the sulfate is primarily ettringite with lesser amounts of monosulfate.

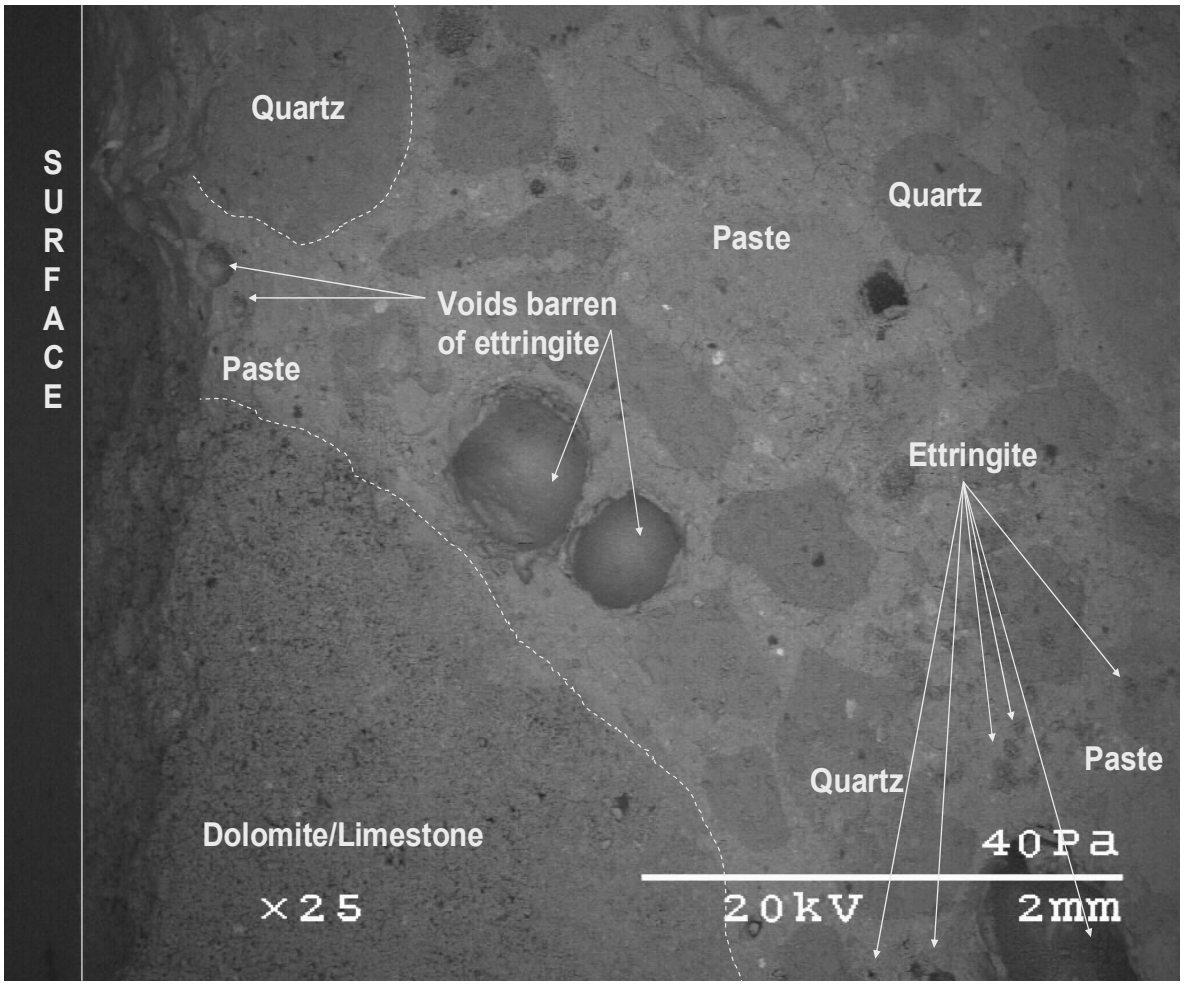

Figure 7. SEM micrograph of roof sample Q3TM showing a pathway of air voids close to the sample surface that are devoid of ettringite. At a distance of approximately 4 mm from the surface, ettringite remains in the air voids showing the distance the chelating phosphonate solution penetrated.

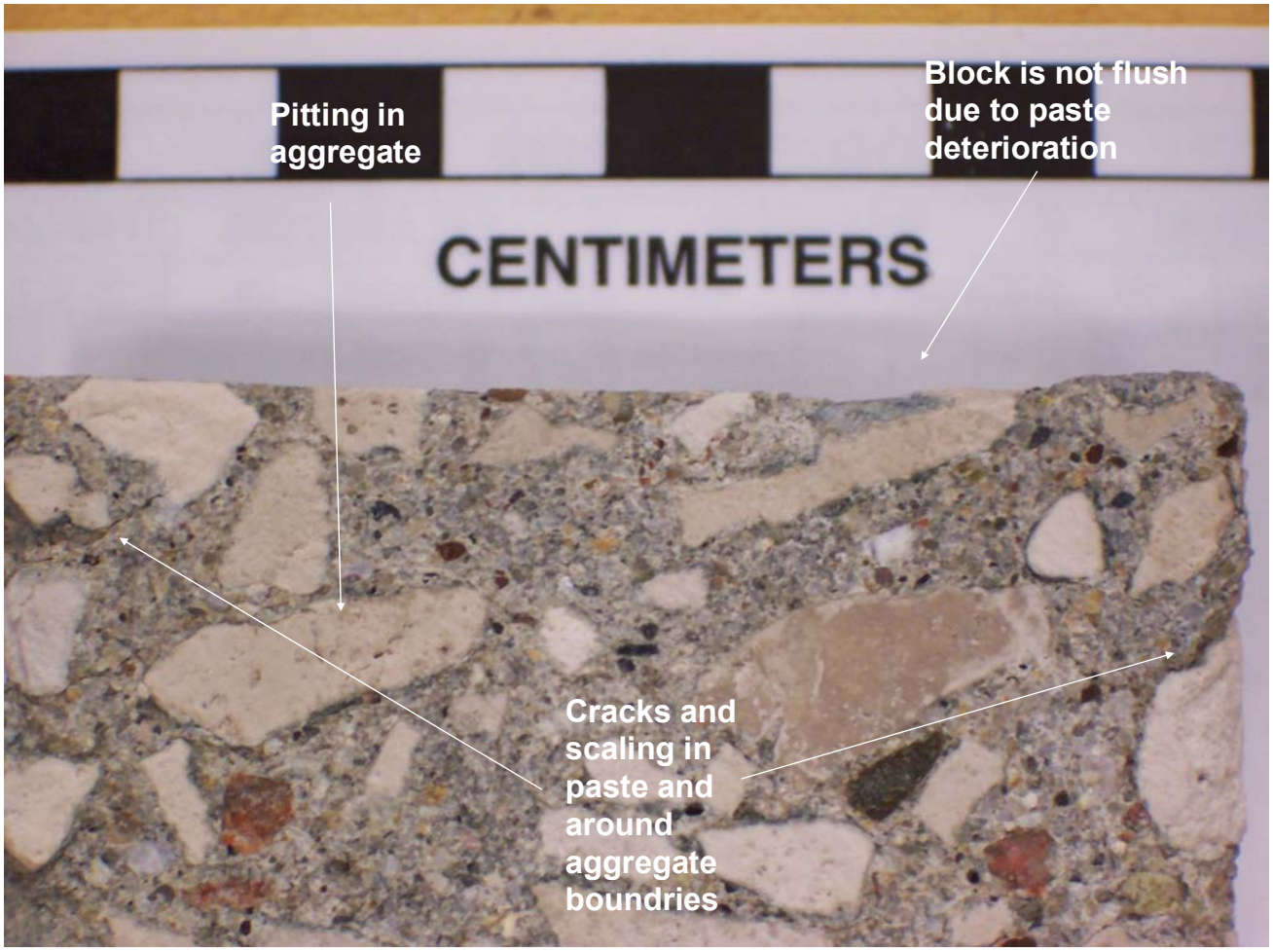

Figure 8. Sample Q3TB was subject to freeze-thaw cycling and application of Dequest 2060S over a one year period and shows signs of pitting, scaling, and cracking.

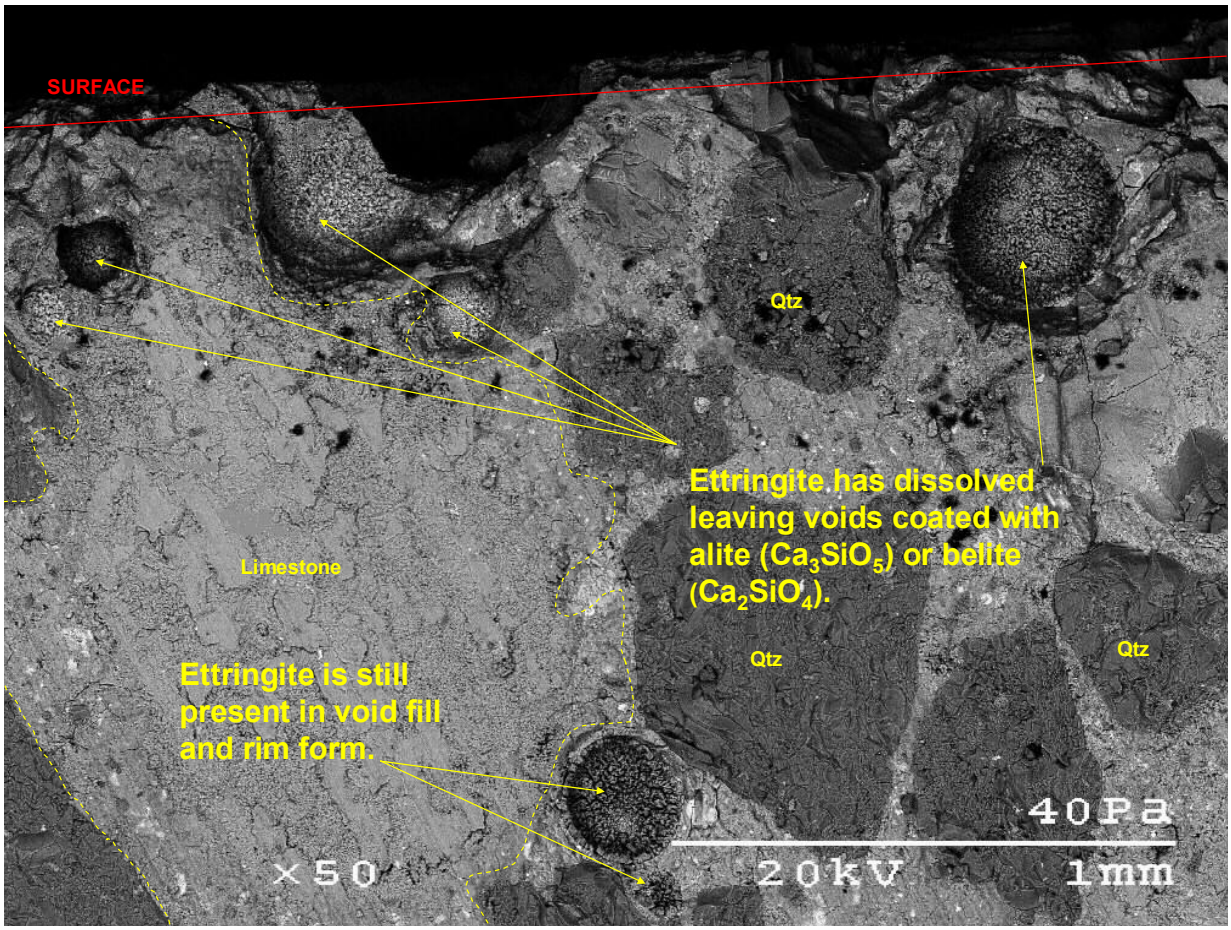

Figure 9. SEM micrograph of sample Q3TB. Near the surface, air voids contain no ettringite but instead trace amounts of alite and belite. At a distance of 2 mm from the surface, euhedral crystals of ettringite line the walls of the air voids.

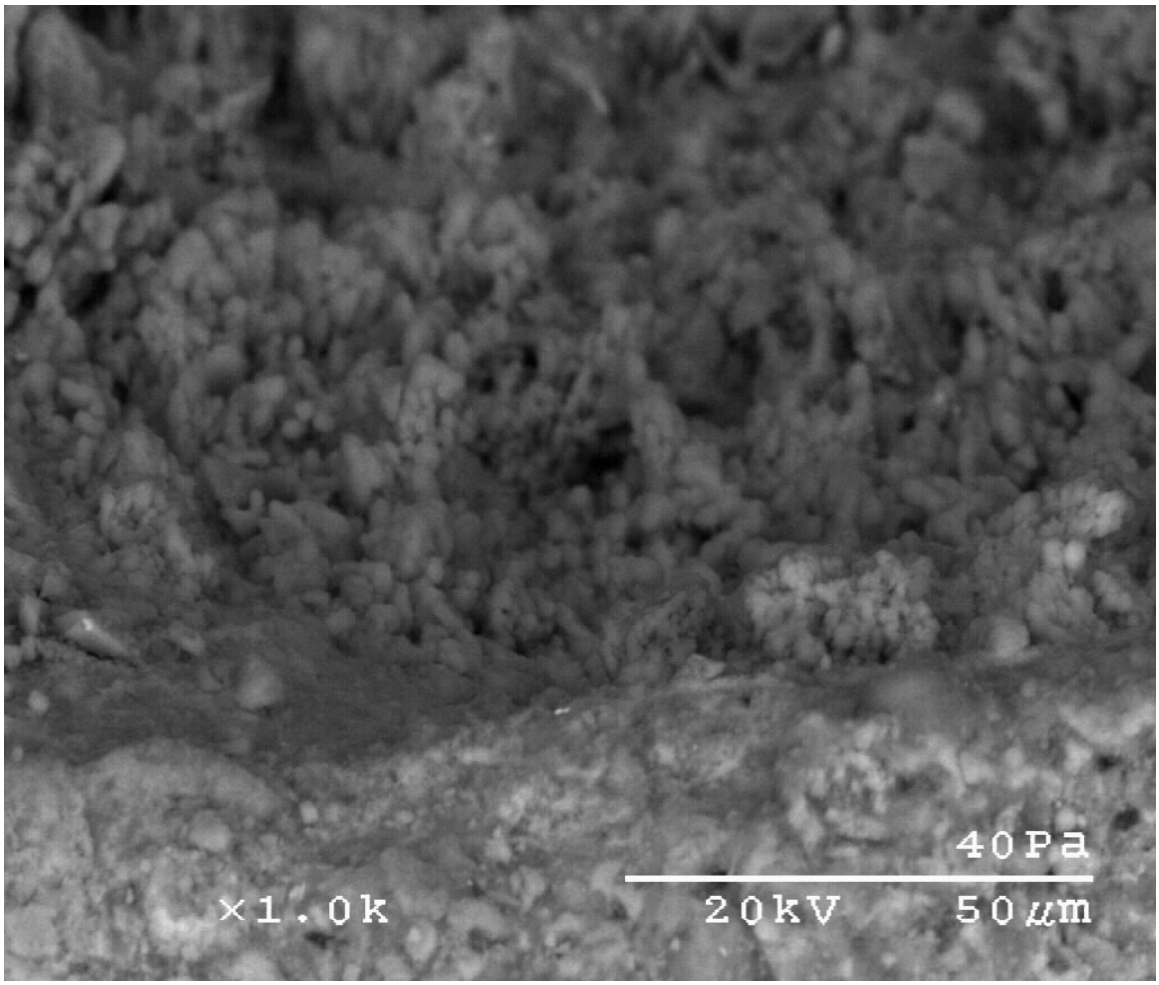

Figure 10. SEM micrograph of stunted ettringite crystals (~10-15 µm in length) in sample H4TB

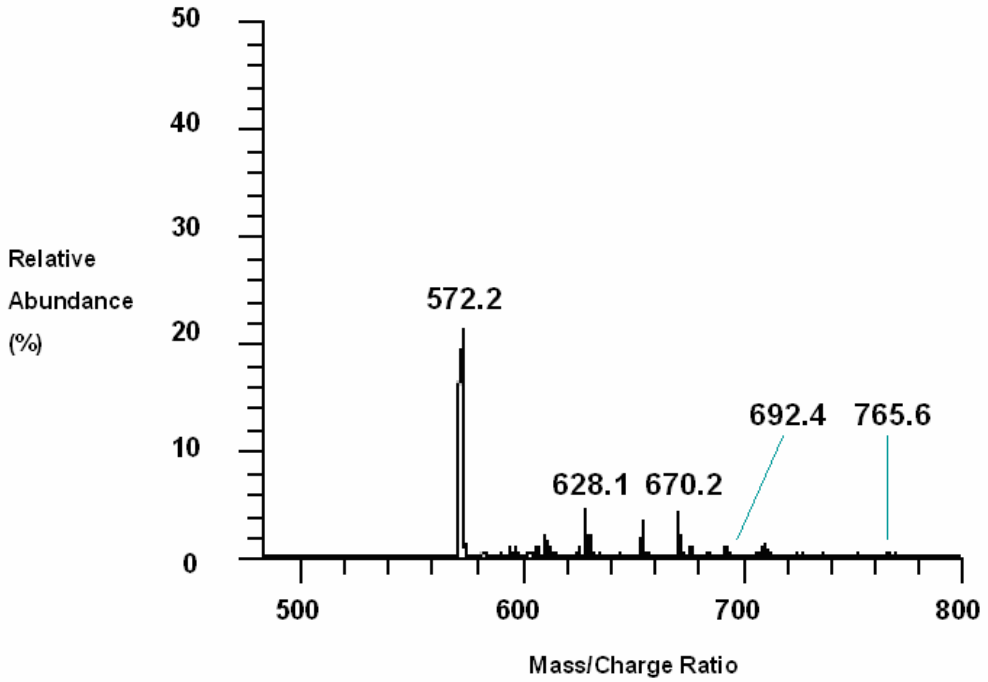

Figure 11. Electrospray mass spectrometry spectrum in negative ionization mode of deprotonated DTPMP molecule (molecular weight = 572.2), with a Ca^{2+} and a water molecule adsorbed onto the phosphonate molecule (molecular weight = 628.1) and other unidentifiable species.

Appendix A: General information on concrete cores used in roof and laboratory experiments

Samp. #	Iowa Location	Project ID #	Year Built	Mile Post	Sample #	Core Locations	Lane	Core Station	Core Mile Post	Quarry Location
H1T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H1T**	208+89 to 189+72	WB	WB 136+00	17	Eagle City Fm
HIB	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**HIB**	208+89 to 189+72	WB	WB 136+00	17	Eagle City Fm
H2T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H2T**	189+72 to 170+76	WB	WB 136+00	17	Eagle City Fm
H2B	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H2B**	189+72 to 170+76	WB	WB 136+00	17	Eagle City Fm
H3T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H3T**	208+89 to 189+72	WB	WB 136+00	17	Eagle City Fm
H3B	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H3B**	208+89 to 189+72	WB	WB 136+00	17	Eagle City Fm
H4T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H4T**	189+72 to 170+76	WB	WB 136+00	17	Eagle City Fm
H4B	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H4B**	189+72 to 170+76	WB	WB 136+00	17	Eagle City Fm
H5T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H5T**	982+00 to 995+53	EB	EB 994+00	13	Eagle City Fm
H5B	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H5B**	982+00 to 995+53	EB	EB 994+00	13	Eagle City Fm
H6T	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H6T**	995+53 to 13+00	EB	EB 994+00	13	Eagle City Fm
H6B	SH163 Polk/Jasper Co.	RP-163-1(50)--16-77	1992	12.36 to 17.01	**H6B**	995+53 to 13+00	EB	EB 994+00	13	Eagle City Fm
E1T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E1T**	260+00 to 238+40	WB	WB 210+00	208.7	Eagle City Fm
E1B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E1B**	260+00 to 238+40	WB	WB 210+00	208.7	Eagle City Fm
E2T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E2T**	231+70 to 201+65	WB	WB 210+00	208.7	Eagle City Fm
E2B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E2B**	231+70 to 201+65	WB	WB 210+00	208.7	Eagle City Fm
E3T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E3T**	260+00 to 238+40	WB	WB 210+00	208.7	Eagle City Fm
E3B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E3B**	260+00 to 238+40	WB	WB 210+00	208.7	Eagle City Fm
E4T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E4T**	231+70 to 201+65	WB	WB 210+00	208.7	Eagle City Fm
E4B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E4B**	231+70 to 201+65	WB	WB 210+00	208.7	Eagle City Fm
E5T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E5T**	?	WB	WB 210+00	208.7	Eagle City Fm
E5B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E5B**	?	WB	WB 210+00	208.7	Eagle City Fm
E6T	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E6T**	?	WB	WB 210+00	208.7	Eagle City Fm
E6B	I-80 Iowa Co.	IR-80-6(157)205--12-4	1992	204.80 to 209.65	**E6B**	?	WB	WB 210+00	208.7	Eagle City Fm
Q2T	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q2T**	1323+08 to 1316+50	SB	SB 1317+00	58	North Hill Group
Q2B	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q2B**	1323+08 to 1316+50	SB	SB 1317+00	58	North Hill Group
Q3T	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q3T**	1328+50 to 1324+30	SB	SB 1317+00	58	North Hill Group
Q3B	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q3B**	1328+50 to 1324+30	SB	SB 1317+00	58	North Hill Group
Q4T	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q4T**	1323+08 to 1316+50	SB	SB 1317+00	58	North Hill Group
Q4B	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q4B**	1323+08 to 1316+50	SB	SB 1317+00	58	North Hill Group
Q5T	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q5T**	1223+50 to 1243+53	NB	NB 1268+00	57	North Hill Group
Q5B	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q5B**	1223+50 to 1243+53	NB	NB 1268+00	57	North Hill Group
Q6T	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q6T**	1264+25 to 1281+00	NB	NB 1268+00	57	North Hill Group

Samp. #	Iowa Location	Project ID #	Year Built	Mile Post	Samp. #	Core Locations	Lane	Core Station	Core Mile Post	Quarry Location
Q6B	US165 Polk Co.	NHS-500-1(96)--19-77	1997	55.87 to 60.11	**Q6B**	1264+25 to 1281+00	NB	NB 1268+00	57	North Hill Group
P1T	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P1T**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P1B	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P1B**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P3T	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P3T**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P3B	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P3B**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P4T	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P4T**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P4B	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P4B**	1001+40 to 1040+45	EB	EB 1009+00	51	Eagle City Fm
P5T	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P5T**	1214+48 to 1187+56	EB	WB 1191+00	55	Eagle City Fm
P5B	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P5B**	1214+48 to 1187+56	EB	WB 1191+00	55	Eagle City Fm
P6T	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P6T**	1214+48 to 1187+56	EB	WB 1191+00	55	Eagle City Fm
P6B	SH163 Mahaska Co.	NHS-163-4(22)--2R-62	1997	44.99 to 54.78	**P6B**	1214+48 to 1187+56	EB	WB 1191+00	55	Eagle City Fm
F1TJ	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F1TJ**	528+30 to 525+47	FW	NB 508+00	51	Hopington Fm
F1BJ	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F1BJ**	528+30 to 525+47	FW	NB 508+00	51	Hopington Fm
F2BMS	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F2BMS**	525+47 to 511+55	FW	NB 508+00	51	Hopington Fm
F3TJ	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F3TJ**	528+30 to 525+47	FW	NB 508+00	51	Hopington Fm
F3BJ	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F3BJ**	528+30 to 525+47	FW	NB 508+00	51	Hopington Fm
F4TMS	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F4TMS**	525+47 to 511+55	FW	NB 508+00	51	Hopington Fm
F4BMS	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F4BMS**	525+47 to 511+55	FW	NB 508+00	51	Hopington Fm
F5T	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F5T**	502+45 to 502+00	FW	NB 482+00	51	Hopington Fm
F5B	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F5B**	502+45 to 502+00	FW	NB 482+00	51	Hopington Fm
F5B2	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F5B2**	502+45 to 502+00	FW	NB 482+00	51	Hopington Fm
F6T	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F6T**	502+00 to 500+85	FW	NB 482+00	51	Hopington Fm
F6B	SH150 Buchanan Co.	F-150-3(42)--20-10	1992	49.20 to 51.35	**F6B**	502+00 to 500+85	FW	NB 482+00	51	Hopington Fm
O2T	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O2T**	243+61 to 277+26	NB	SB 287+00	35	Scotch Grove Fm
O2B	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O2B**	243+61 to 277+26	NB	SB 287+00	35	Scotch Grove Fm
O3T	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O3T**	284+26 to 297+07	SB	SB 287+00	35	Scotch Grove Fm
O3B	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O3B**	284+26 to 297+07	SB	SB 287+00	35	Scotch Grove Fm
O4T	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O4T**	243+61 to 277+26	NB	SB 287+00	35	Scotch Grove Fm
O4B	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O4B**	243+61 to 277+26	NB	SB 287+00	35	Scotch Grove Fm
O5T	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O5T**	?	?	SB 287+00	35	Scotch Grove Fm
O5B	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O5B**	?	?	SB 287+00	35	Scotch Grove Fm
O6T	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O6T**	?	?	SB 287+00	35	Scotch Grove Fm
O6B	US151 Linn Co.	NHS-151-3(97)--19-57	1997	33.48 to 36.68	**O6B**	?	?	SB 287+00	35	Scotch Grove Fm

Appendix B: Summary of etrographic observations of concrete core samples

Sample #	Lime/Dolo Stone	Ag. Grain Size (mm)	Grain Shape	Aggregate Rims (Y or N) & Description	Flyash or Slag	Void (Paste) %	Ettringite in Voids (Description)	Cracks (Where)
H1T	Dolo/Lime	0.03 to 0.09	An to Sub	Partial and Complete Rims Into Paste	None	5%	Some Rim	Large crack in paste
HIB	Dolo/Lime	0.06 to 0.12	An to Sub	Partial Rims, Some Into Paste	None	5%	Some Rim	Fine and medium aggregate
H2T	Dolo/Lime	0.03 to 0.20	Sub	None	None	5%	None	Large cracks in paste and fine & coarse aggregate
H2B	Dolo/Lime	0.04 to 0.10	Sub	Partial and Complete Rims	None	5%	Rim and Void Filled	Fine aggregate
H3T	Dolo/Lime	0.05 to 0.22	Sub	Partial and Complete Rims	None	5%	Rim and Small Void Filled	Fine aggregate
H3B	Dolo/Lime	0.02 to 0.13	Sub to Euh	Partial Rims	None	5%	Rim and Small Void Filled	Coarse aggregate
H4T	Dolo/Lime	0.02 to 0.10	Sub to Euh	Partial Rims	None	5%	Rim and Small Void Filled	Coarse aggregate
H4B	Dolo/Lime	0.02 to 0.10	Sub to Euh	Partial Rims	None	5%	Rim and Small Void Filled	None
H5T	Dolo/Lime	0.05 to 0.18	Sub to Euh	Partial and Complete Rims	None	5%	Rim and Small Void Filled	Large crack in paste/Coarse aggregate
H5B	Dolo/Lime	0.05 to 0.15	Sub to Euh	Partial Rims, Some Into Paste	None	5%	Rim and Small Void Filled	None
H6T	Dolo/Lime	0.02 to 0.12	Sub to Euh	Partial Rims	None	5%	Large Rims Going to Void Filled	Fine aggreagte
H6B	Dolo/Lime	0.02 to 0.13	Sub	Partial Rims	None	5%	Rim and Small Void Filled	Fine & coarse aggregate
E1T	Dolo/Lime	0.05 to 0.10	Sub	Partial and Complete Rims Into Paste	None	5%	Rim and Small Void Filled	Fine & coarse aggregate
E1B	Dolo/Lime	0.04 to 0.14	An to Sub	Partial Rims	None	5%	Rim and Void Filled	Fine aggregate
E2T	Dolo/Lime	0.03 to 0.18	Sub to Euh	Partial and Complete Rims Into Paste	None	5%	Small Void Filled	Large cracks through fine aggregate and paste
E2B	Dolo/Lime	0.02 to 0.13	Sub to Euh	Partial Rims	None	5%	Rim and Void Filled	Large crack around large void space
E3T	Dolo/Lime	0.02 to 0.18	Sub to Euh	Partial and Complete Rims Into Paste	None	5%	Small Void Filled	Large crack in paste
E3B	Dolo/Lime	0.05 to 0.10	Sub	Partial Rims	None	5%	Rim and Void Filled	Large crack in paste
E4T	Dolo/Lime	0.10	Sub	Partial and Complete Rims	None	5%	Rim and Small Void Filled	None
E4B	Dolo/Lime	0.02 to 0.10	Sub to Euh	Partial and Complete Rims	None	5%	Rim and Small Void Filled	None
E5T	Dolo/Lime	0.02 to 0.12	Sub	Partial and Complete Rims	None	5%	Some Rim and Small Void Filled	Fine aggregate
E5B	Dolo/Lime	0.02 to 0.11	Sub	Partial and Complete Rims	None	5%	Rim and Void Filled	Coarse aggregate
E6T	Dolo/Lime	0.04 to 0.12	Sub to Euh	Partial and Complete Rims	None	5%	Rim and Small Void Filled	Coarse aggregate
E6B	Dolo/Lime	0.02 to 0.05	Sub	Partial and Complete Rims	None	5%	Rim and Void Filled	None
Q2T	Lime	0.10	Sub to Euh	None	None	5%	Rim	Fine aggregate
Q2B	Lime	0.05 to 0.25	Sub to Euh	Partial and Complete Rims	None	5%	Some Rim	Coarse aggregate
Q3T	Lime	0.12	Sub to Euh	Partial Rims, Some Into Paste	None	5%	None	Large crack in paste
Q3B	Lime	0.03 to 0.15	Sub	Partial Rims, Some Into Paste	None	5%	Rim	None
Q4T	Lime	0.02 to 0.25	Sub	Partial Rims, Some Into Paste	None	5%	Small Void Filled	Large crack in paste/Coarse aggregate
Q4B	Lime	0.02 to 0.10	An to Sub	Partial Rims	None	5%	Rim and Void Filled	None
Q5T	Lime	0.05 to 0.28	Sub to Euh	Partial Rims	None	5%	Some Rim and Small Void Filled	None
Q5B	Lime	0.01 to 0.08	An to Sub	Partial and Complete Rims	None	5%	None	Coarse aggregate

Sample #	Lime/Dolo Stone	Ag. Grain Size (mm)	Grain Shape	Aggregate Rims (Y or N) & Description	Flyash or Slag	Void (Paste) %	Ettringite in Voids (Description)	Cracks (Where)
Q6T	Lime	0.12	Sub to Euh	Partial Rims, Some Into Paste	None	5%	Some Rim and Small Void Filled	Coarse aggregate
Q6B	Limestone	0.05 to 0.18	An to Sub	Complete Rims	None	5%	Some Rim	None
P1T	Dolo/Lime	0.05	An to Sub	Partial Rims, Some Into Paste	None	5%	Some Rim and Small Void Filled	Fine aggregate
P1B	Dolo/Lime	0.04 to 0.18	An to Sub	Partial and Complete Rims	None	5%	Rim and Void Filled	Coarse aggregate
P3T	Dolo/Lime	0.02 to 0.14	Sub	Partial and Complete Rims	None	5%	Small Void Filled	Coarse aggregate
P3B	Dolo/Lime	0.03 to 0.10	Sub	Partial and Complete Rims	None	5%	Small Void Filled	Coarse aggregate
P4T	Dolo/Lime	0.05 to 0.10	An to Sub	Partial and Complete Rims	None	5%	Some Rim and Small Void Filled	Coarse aggregate
P4B	Dolo/Lime	0.02 to 0.10	An to Sub	Partial and Complete Rims Into Paste	None	5%	Small Void Filled	Coarse aggregate
P5T	Dolo/Lime	0.02 to 0.12	An to Sub	Complete Rims	None	5%	Some Rim and Small Void Filled	None
P5B	Dolo/Lime	0.02 to 0.08	An to Sub	Partial and Complete Rims Into Paste	None	5%	Rim and Void Filled	Coarse aggregate
P6T	Dolo/Lime	0.02 to 0.06	An to Sub	Partial and Complete Rims Into Paste	None	5%	Some Rim and Small Void Filled	Coarse aggregate
P6B	Dolo/Lime	0.02 to 0.07	An to Sub	Partial and Complete Rims	None	5%	Rim and Small Void Filled	Coarse aggregate
F1TJ	Dolo	0.03 to 0.10	An to Sub	Partial and Complete Rims	None	5%	Rim	Coarse aggregate
F1BJ	Dolo	0.04 to 0.10	An to Sub	Partial Rims, Some Into Paste	None	5%	Rim and Small Void Filled	Fine aggregate
F2BMS	Dolo	0.04 to 0.08	An	None	None	5%	Rim and Small Void Filled	None
F3TJ	Dolo	0.03 to 0.10	Sub	Partial and Complete Rims Into Paste	None	5%	None	Large cracks in paste/Coarse aggregate
F3BJ	Dolo	0.04 to 0.10	An to Sub	Complete Rims	None	5%	Rim and Void Filled	None
F4TMS	Dolo	0.04 to 0.10	Sub	Complete Rims, Some Into Paste	None	5%	None	Large crack in paste
F4BMS	Dolo	0.03 to 0.10	An to Sub	Partial Rims	None	5%	Rim and Void Filled	None
F5T	Dolo	0.03 to 0.08	An to Sub	Partial and Complete Rims Into Paste	None	5%	None	Large crack in paste
F5B	Dolo	0.04 to 0.08	An to Sub	Partial Rims	None	5%	Rim and Void Filled	None
F5B2	Dolo	0.04 to 0.09	An	Partial and Complete Rims Into Paste	None	5%	Void Filled	None
F6T	Dolo	0.03 to 0.08	An to Sub	Partial and Complete Rims Into Paste	None	5%	Void Filled	Large crack in paste
F6B	Dolo	0.03 to 0.09	An	Partial Rims	None	5%	Rim and Void Filled	None
O2T	Lime	0.02 to 0.13	An to Sub	Partial Rims, Some Into Paste	Flyash	8%	None	Fine & coarse aggregate
O2B	Lime	0.02 to 0.08	An to Sub	None	Flyash	8%	None	Fine aggregate
O3T	Lime	0.03 to 0.12	An to Sub	Partial Rims	Flyash	8%	None	Large cracks in paste/Coarse aggregate
O3B	Lime	0.02 to 0.08	An to Sub	Partial Rims	Flyash	8%	None	Coarse aggregate
O4T	Lime	0.02 to 0.10	An to Sub	Partial Rims	Flyash	8%	None	None
O4B	Lime	0.02 to 0.07	An to Sub	Partial Rims, Some Into Paste	Flyash	8%	None	None
O5T	Lime	0.02 to 0.10	Sub	Partial Rims	Flyash	8%	None	Coarse aggregate
O5B	Lime	0.02 to 0.05	An to Sub	Partial Rims	Flyash	8%	None	Coarse aggregate
O6T	Lime	0.02 to 0.12	Sub	Partial and Complete Rims Into Paste	Flyash	8%	None	None
O6B	Lime	0.02 to 0.08	Sub	None	Flyash	8%	None	None

Appendix C: Percentage of S-bearing minerals (pyrite and gypsum) and members of the system Fe-O-H in roadway cores used in roof and laboratory experiments

Sample #	Pyrite	Gypsum	Magnitite	Hematite	Goethite	Sample #	Pyrite	Gypsum	Magnitite	Hematite	Goethite
H1T	0.40%	x	0.10%	x	0.20%	**Q6B**	0.05%	2.00%	0.10%	x	Trace
HIB	0.40%	2.00%	0.20%	0.05%	0.20%	**P1T**	Trace	1.00%	0.50%	x	x
H2T	0.30%	x	0.20%	0.02%	0.10%	**P1B**	Trace	x	0.25%	x	x
H2B	0.30%	2.00%	0.30%	x	0.20%	**P3T**	Trace	x	0.05%	x	x
H3T	0.30%	x	0.20%	0.01%	0.10%	**P3B**	0.05%	0.50%	0.10%	x	Trace
H3B	0.30%	0.50%	0.10%	0.02%	0.20%	**P4T**	0.01%	x	0.05%	x	Trace
H4T	0.30%	x	0.10%	0.01%	0.05%	**P4B**	0.01%	x	0.05%	x	Trace
H4B	0.20%	x	0.20%	x	0.03%	**P5T**	0.01%	1.00%	0.05%	Trace	x
H5T	0.10%	x	0.10%	x	0.01%	**P5B**	0.05%	x	0.07%	Trace	x
H5B	0.30%	x	0.30%	x	0.10%	**P6T**	0.01%	x	0.05%	x	Trace
H6T	0.10%	x	0.20%	0.10%	0.02%	**P6B**	Trace	2.00%	0.05%	x	x
H6B	2.00%	x	0.30%	x	0.01%	**F1TJ**	Trace	x	0.04%	Trace	0.05%
E1T	0.20%	x	0.20%	x	x	**F1BJ**	x	x	0.01%	Trace	x
E1B	0.10%	x	0.20%	0.10%	x	**F2BMS**	x	x	Trace	x	Trace
E2T	0.10%	x	0.10%	0.05%	x	**F3TJ**	x	x	0.01%	x	0.01%
E2B	0.10%	x	0.20%	0.05%	x	**F3BJ**	x	x	0.03%	Trace	x
E3T	0.20%	0.50%	0.10%	0.02%	x	**F4TMS**	x	x	0.03%	x	Trace
E3B	0.10%	x	0.10%	0.02%	x	**F4BMS**	x	x	0.01%	x	x
E4T	0.02%	0.50%	0.10%	0.05%	x	**F5T**	Trace	x	0.02%		0.01%
E4B	0.07%	x	0.02%	0.01%	x	**F5B**	x	x	0.01%	Trace	Trace
E5T	0.10%	x	0.02%	0.01%	0.05%	**F5B2**	x	x	0.01%	Trace	x
E5B	0.10%	0.50%	0.02%	0.02%	x	**F6T**	x	2.00%	0.02%	Trace	Trace
E6T	0.01%	2.00%	0.05%	x	x	**F6B**	Trace	x	0.01%	Trace	x
E6B	0.07%	x	0.10%	0.01%	x	**O2T**	0.01%	x	Trace	Trace	x
Q2T	0.07%	x	0.10%	0.10%	0.02%	**O2B**	Trace	x	0.01%	Trace	x
Q2B	0.10%	0.50%	0.50%	x	x	**O3T**	0.01%	x	0.01%	Trace	Trace
Q3T	0.05%	x	0.07%	x	0.01%	**O3B**	0.01%	x	0.01%	x	Trace
Q3B	0.05%	x	0.05%	x	x	**O4T**	Trace	0.25%	Trace	x	x
Q4T	0.05%	x	0.07%	x	x	**O4B**	Trace	x	Trace	x	x
Q4B	0.07%	0.25%	0.05%	x	x	**O5T**	Trace	0.25%	Trace	x	x
Q5T	0.05%	x	0.05%	0.01%	x	**O5B**	0.05%	x	0.01%	Trace	x
Q5B	0.05%	x	0.01%	x	x	**O6T**	Trace	x	Trace	x	x
Q6T	0.02%	x	0.20%	0.01%	x	**O6B**	Trace	x	0.01%	x	x

Appendix D: 1992 core sample cement mix information

ID	Year	Project Number	Roadway	County	Contractor	Max./Min. Temp	Mix Type
E	92	IR-80-6(157)205--12-48	I-80	Iowa	Fred Carlson	85/55	C-3WR-C
						77/54	C-3WR-C
						86/65	C-3WR-C
F	91	F-150-3(42)--20-10	SH-150	Buchanan	Manatt's	70/55	C-3WR-C
						89/60	C-3WR-C
						65/50	C-3WR-C
						65/50	C-3WR
						65/50	C-3WR
						50/35	C-3WR
	92					47/38	C-3WR-C
H	92	RP-163-1(50)--16-77	SH-163	Polk/Jasper	Cedar Valley	84/56	C-4WR-C
						86/68	C-4WR-C
						82/68	C-4WR-C
						57/46	C-4WR
						54/47	C-4WR

ID	Cement	Fly Ash	Fine Aggregate	Coarse Aggregate	Water Reducer	Air Entraining Agent
E	Buffalo IA (I)	Ottumwa (C)	Disterhoff (A48508)	Sully (A50002)	Sika Plastocrete 161	Sika AER
	Buffalo IA (I)	Ottumwa (C)	Disterhoff (A48508)	Sully (A50002)	Sika Plastocrete 161	Sika AER
	Buffalo IA (I)	Ottumwa (C)	Disterhoff (A48508)	Sully (A50002)	Sika Plastocrete 161	Sika AER
F	Mason City IA (LH I)	Louisa (C)	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (LH I)	Louisa (C)	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (LH I)	Louisa (C)	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (LH I)	None	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (LH I)	None	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (LH I)	None	Hoffman (A10510)	Hazleton (A10010)	Protex PDA25-DP	Protex AES
	Mason City IA (HN I)	Louisa (C)	Randalia (A33510)	Hazleton (A10010)	Prokrete N-3	Conchem AES
H	Mason City IA (HN I)	Ottumwa (C)	Colfax (A50502)	Sully (A50002)	WRDA-82	Dara-Vair R
	Mason City IA (HN I)	Ottumwa (C)	Colfax (A50502)	Sully (A50002)	WRDA-82	Dara-Vair R
	Mason City IA (HN I)	Ottumwa (C)	Colfax (A50502)	Sully (A50002)	WRDA-82	Dara-Vair R
	Mason City IA (HN I)	None	Colfax (A50502)	Sully (A50002)	WRDA-82	Dara-Vair R
	Mason City IA (HN I)	None	Colfax (A50502)	Sully (A50002)	WRDA-82	Dara-Vair R

Appendix E: 1997 core sample cement mix information

ID	Year	Project Number	Roadway	County	Contractor	Max./Min. Temperature	Mix Type
O	97	NHS-151-3(97)--19-57	US-151	Linn	Allied Construction	91/67	C-3WR-C10
						77/53	C-3WR-C10
						83/59	C-3WR-C10
P	97	NHS-163-4(22)--2R-62	SH-163	Mahaska	Fred Carlson	82/56	C-3WR-C20
						75/56	C-3WR-C20
Q	97	NHS-137-3(19)--19-62	SH-137	Mahaska	Manatt's	46/23	C-3-C20
						46/23	C-3-C20
						90/70	C-3WR-C20
						87/68	C-3WR-C20

ID	Cement	Fly Ash	Fine Aggregate	Coarse Aggregate	Water Reducer	Air Entraining Agent
O	Mason City IA (HN IS)	Louisa (C)	Ivanhoe (A57520)	Bowser-Springville (A57008)	Sika Plastocrete 161	Daravair 1000
	Mason City IA (HN IS)	Louisa (C)	Ivanhoe (A57520)	Bowser-Springville (A57008)	Sika Plastocrete 161	Daravair 1000
	Mason City IA (HN IS)	Louisa (C)	Ivanhoe (A57520)	Bowser-Springville (A57008)	Sika Plastocrete 161	Daravair 1000
P	Louisville NE (I/II)	Council Bluffs #3 (C)	New Harvey (A63512)	Sully (A50002)	Sika Plastocrete 161	Sika AEA-15
	Louisville NE (I/II)	Ottumwa (C)	New Harvey (A63512)	Sully (A50002)	Sika Plastocrete 161	Sika AEA-15
Q	Mason City IA (HN I/II)	Louisa (C)	New Harvey (A63512)	Sully (A50002)	None	Conchem Air
	Mason City IA (HN I/II)	Louisa (C)	New Harvey (A63512)	Sully (A50002)	None	Conchem Air
	Mason City IA (HN I/II)	Louisa (C)	New Harvey (A63512)	Sully (A50002)	Conchem 25DP **	Conchem Air
	Mason City IA (HN I/II)	Louisa (C)	New Harvey (A63512)	Sully (A50002)	Conchem 25DP **	Conchem Air

Appendix F: U.S. 20 core sample cement mix information

Eastbound US 20 Built 1999 QMC Mix Design

Cement Type IS	0.093
Fly Ash	0.019
Coarse	0.32
Intermediate 1/2"	0.057
Fine	0.308
Water	0.133
Air	0.07

Westbound US 20 Built 1991 C-3WR-C15

Cement Type I	0.092
Fly Ash	0.019
Coarse	0.375
Fine	0.308
Water	0.146
Air	0.06