

PCC Pavement Deterioration and Expansive Mineral Growth

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In order to evaluate the importance of newly-formed minerals in the premature deterioration of Iowa highway concrete, a two-phase study was undertaken. In the first phase, we performed petrographic and SEM/EDAX analyses to determine chemical and mineralogical changes in the aggregate and cement paste of samples taken from Iowa concrete highways that showed premature deterioration. In the second phase, we experimentally simulated environmental changes occurring in highway concrete after different deicer chemicals were applied in order to evaluate the role of deicers in premature deterioration. In highways exhibiting premature concrete deterioration, ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$, completely fills many small voids and lines the walls of larger voids. Microscopic ettringite is also commonly disseminated throughout the paste of many samples. Severe cracking of cement paste is usually associated with ettringite locations, and strongly suggests that ettringite contributed to deterioration. Pyrite, FeS_2 , is present in coarse/fine aggregates in several concretes. Sulfate ions released by its oxidation contribute to ettringite formation. In poorly performing concretes containing reactive dolomite aggregate, brucite, $\text{Mg}(\text{OH})_2$, resulting from partial dedolomitization of the aggregate, was most common. No cracking was observed to be spatially associated with brucite, but most brucite crystals are microscopic in size and widely disseminated in the cement paste of less durable concretes. Expansion stresses associated with its growth at many microlocations may be relieved by cracking at weaker sites in the concrete. In the experimental phase of the study we found that each deicer salt can cause characteristic concrete deterioration by altering dedolomitization rims at the coarse-aggregate paste interface, by altering cement paste, and/or by forming new expansive minerals in the paste. Magnesium in deicer solutions produces the most severe paste deterioration by forming non-cementitious magnesium silicate hydrate and brucite. Chloride in deicer solutions promotes decalcification of paste and alters ettringite to chloroaluminate. Acetate seems to accentuate Mg-induced deterioration. Magnesium chloride, calcium magnesium acetate ($\text{Ca}_3\text{Mg}_2\text{Ac}$), and magnesium acetate were the most deleterious. Key words: concrete, deterioration, deicers, highways.

INTRODUCTION AND PROBLEM STATEMENT

Iowa highways constructed of concrete containing carbonate coarse aggregate from certain quarries sometimes have service lives of less than 10 years. Premature deterioration can be caused by many

factors. The current report investigates the role that potentially expansive minerals have in their premature deterioration and whether deicer applications accentuate deterioration.

Considerable progress has been made in reducing premature failure of highway concrete, but problem concretes such as those studied here continue to fail prematurely. One area of uncertainty about the causes of failure is the significance of newly-formed minerals in concrete. Two common secondary minerals, brucite, $\text{Mg}(\text{OH})_2$ and ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ or $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, are often implicated in premature deterioration, and the cause of deterioration is often attributed to expansion and cracking related to their growth. The importance of expansion in the deterioration of concrete by growth of these minerals is still controversial and not accepted by all workers (1). Primary ettringite, which grows when concrete is still plastic, easily pushes other materials aside and is not harmful, but ettringite that forms long after concrete has hardened (delayed ettringite) may produce damaging expansive pressures (2). Delayed ettringite formation is especially enhanced by the availability of sulfur, because ettringite's other components, calcium, aluminum, and water are abundant in Portland cement concrete. Sulfur can be derived from gypsum added to the concrete to delay setting, from sulfate-containing ground or surface waters that infiltrate into the concrete, from sulfate impurities in road salt, or from oxidation of sulfide minerals that occur in coarse or fine aggregate.

PROCEDURES

Personnel of the Iowa Department of Transportation collected cores from seven different Iowa concrete highways that contain limestone and/or dolomite coarse aggregate from different sources and have different service records (Table 1). Each of the four-inch diameter concrete highway cores was cut into small rectangular blocks, approximately 2cm x 2cm x 4cm. Similar blocks were cut for use in the experimental phase of the study. Polished thin-sections were made from blocks from the top (1 in. from top of the road surface) and bottom (1 in. from the bottom) portions of each core. Petrographic analyses of thin-sections were conducted with both transmitted and reflected light utilizing a standard petrographic polarizing microscope. These analyses were used to identify specific areas to be studied by scanning electron microscope and to supplement observations of features difficult to observe with scanning electron microscopy such as color changes on coarse aggregate margins.

An Hitachi S 2460 reduced-vacuum scanning electron microscope was used for electron microscopy. Back-scattered images

TABLE 1 Concrete Core Locations and Other Data for Iowa Highway Concretes

Core Location	Year*	Coarse Aggregate Source	Portland Cement
I-35, Cerro Gordo Co.	1974	Portland West quarry, Shellrock Fm.	Northwestern I
US 30, Linn Co.	1981	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Lehigh I
IA 9, Howard Co.	1974	Dotzler quarry, Spillville Fm.	Lehigh I
IA 21, Iowa Co.	1982	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Martin Marietta (?)
US 63, Howard Co.	1971	Nelson quarry, Cedar Valley Fm.	Dewey I
US 20, Dubuque Co.	1988	Sundheim quarry, Hopkinton Fm.	Davenport I
IA 100, Linn Co.	1989	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Continental III
US 63, Tama Co.	1972	Smith quarry, Coralville Member, Cedar Valley Fm.	Lehigh I
US 151, Linn Co.	1947	Paralta quarry, Otis Member, Wapsipinicon Fm.	Mixed (Medusa, Lehigh, Dewey, Atlas, Alpha)
US 218, Benton Co.	1971	Garrison quarry, Coralville Member, Cedar Valley Fm.	Davenport I
US 20, Dubuque Co.	1988	Sundheim quarry, Hopkinton Fm.	Davenport I

*Year the highway was constructed.

were taken and energy dispersive analytical x-ray (EDAX) area mapping was performed for Si, Al, K, Na, O, Ca, Mg, S, Cl, and Fe. EDAX point analyses were obtained at high magnification for qualitative mineral identification. An accelerating voltage of 15 kV was generally used for imaging whereas EDAX point analyses were obtained at 20 kV.

RESULTS AND DISCUSSION

Introduction

The majority of core samples were concretes constructed with dolomite coarse aggregate. Previous research divided them into two groups, durable and non-durable concretes, based on their service records (3,4). The term "durable concrete" was used for the highway concretes that had extended service lives of >40 years before significant deterioration, and "non-durable concrete" was used for concretes with service lives of <16 years. The highway concrete containing Sundheim aggregate (Table 1) is classified as durable; all others were non-durable. Our use of the two terms has no necessary correspondence with ASTM-defined durability. Durability correlates with dolomite coarse aggregate reactivity. Poorly performing concretes contain fine-grained, poorly-crystallized, microporous dolomite that has reacted with surrounding concrete paste to produce dark and light-colored partially-dedolomitized rims surrounding the dolomite aggregate fragments (4).

Part One: Newly Formed Minerals in Iowa Highway Concrete

Abundant brucite and ettringite were observed in most of the highway concretes studied, and large amounts of calcite mineralization occurred in the outer regions of partially dedolomitized dolomite aggregate rims. Ettringite was the most abundant secondary mineral, followed by calcite, and then by brucite. Ettringite and brucite were the only potentially expansive substances identified by petrographic microscope and electron imaging methods.

The abundance and size of brucite crystal masses are closely related to dolomite coarse aggregate reactivity. In highway concretes containing reactive dolomite aggregate, abundant, <20 μm diameter, brucite masses commonly occur in the cement paste near dolomite aggregate/cement paste interfaces (Figure 1). These crystals are not usually associated with void spaces. Larger, irregular micro-nodules are also disseminated in the paste at many locations far from dolomite aggregate particles. The latter occurrence indicates that significant quantities of dolomite-derived Mg^{2+} migrate considerable distances before precipitation. In highway concrete with non-reactive dolomite or limestone aggregate, much fewer and smaller masses of brucite are observed. Brucite occurrences show no obvious spatial correlation with cracks in either cement paste or coarse aggregate.

In our Iowa highway concrete samples, ettringite chiefly occurs in air-entrainment void spaces where it grows as needle-like crystals projecting from the void walls. It occurs in two forms in these air-entrainment voids (Figure 2). The first type is void-fill ettringite

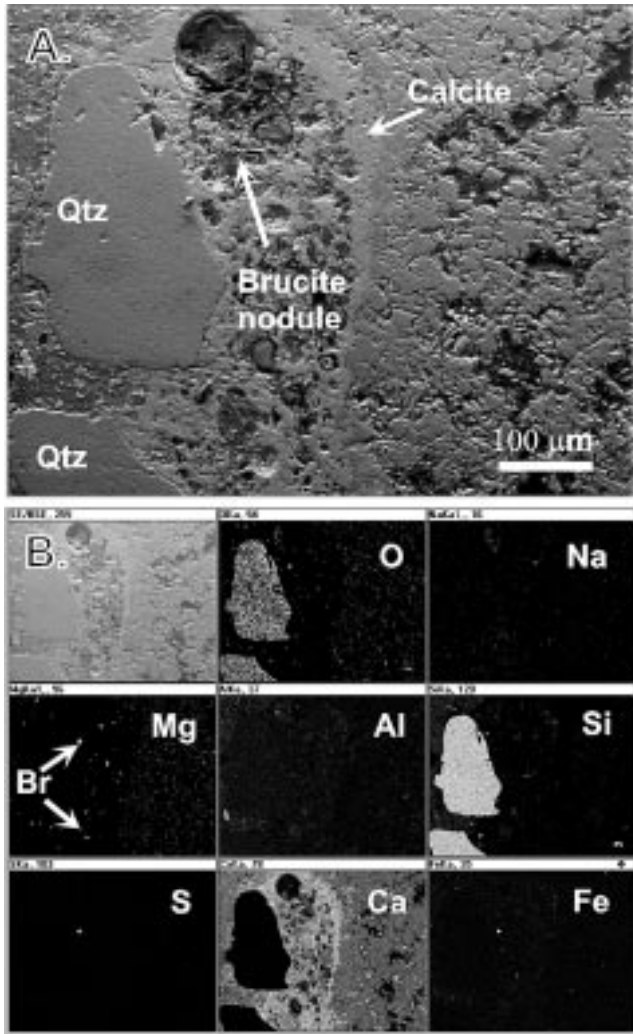


FIGURE 1 Brucite occurrence and calcite enrichment in dolomite coarse aggregate and cement paste. **A.** SEM micrograph. **B.** EDAX area mapping of same area. Note the calcite enrichment in the outer rim of the coarse aggregate fragment in the Ca SEM view and the Ca map, and the brucite (Br) occurrence as shown by small white areas and dots in the Mg map. Qtz = quartz. Dotzler quarry aggregate.

in which the mineral completely fills air-entrainment voids that are usually less than about 100 μm in diameter. Abundant cracks, which are irregular and very disruptive, occur in the ettringite fills. The second type is void-rim ettringite that occurs as rims of ettringite lining the margin of voids. This type usually formed in air-entrainment voids of diameter greater than about 100 μm . Large radially-oriented cracks are prominent throughout the ettringite rims. Some of the cracks in both void-fill and void-rim ettringite continue into the cement paste, but ettringite does not occur in them documenting that ettringite had formed before cracking. Minor amounts of ettringite also fill microscopic interstitial pores in the cement paste and are visible in high-magnification back-scattered SEM images. Very rarely, ettringite occurs in cracks formed along the boundary between quartz fine aggregate particles and cement paste.

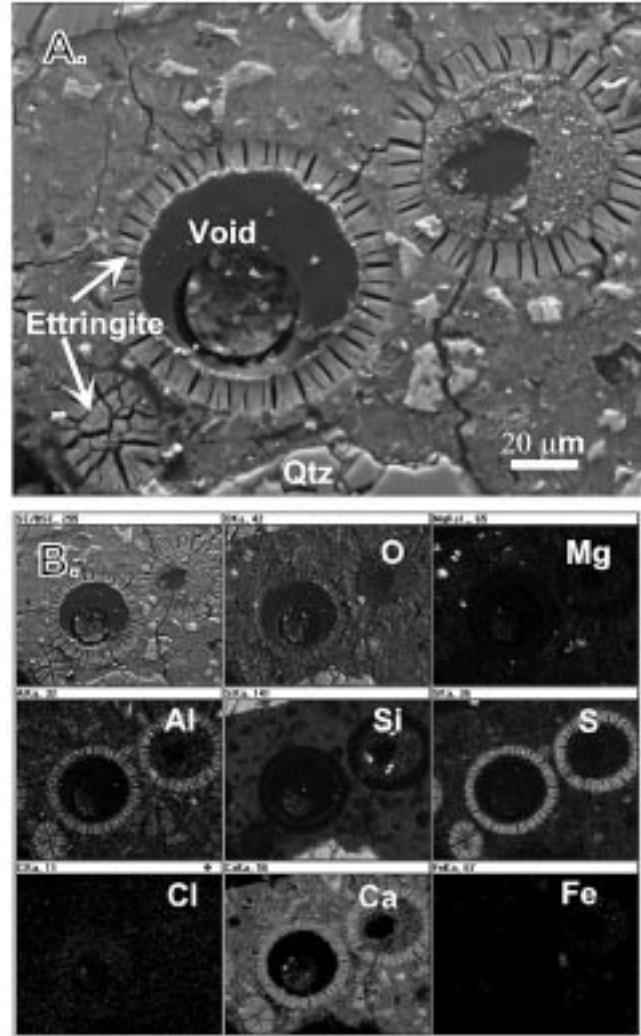


FIGURE 2 Void-rim and void-fill ettringite. **A.** SEM micrograph. **B.** EDAX map of same area. Note the radial cracks associated with the ettringite, and that some of the cracks extend outward into the concrete paste. Brucite crystals can be detected in the upper left and in other areas of the Mg EDAX map. Smith quarry aggregate.

Relationship of Ettringite to Pyrite Inclusions

Sulfate is a necessary component for the formation of ettringite in the cement paste, so that oxidation of sulfide minerals in concrete coarse and fine aggregate may promote delayed ettringite formation (5). Ettringite typically occurs in the cement paste near dolomite aggregates that contain pyrite inclusions, and ettringite abundance is closely associated with the amount of pyrite oxidation as evidenced by the quantities of goethite and/or ferrihydrite associated with the pyrite. Pyrite inclusions in reactive dolomite aggregate are more oxidized than those in non-reactive aggregate because of greater microporosity and finer dolomite crystal sizes in the reactive material that allow oxidizing solutions to react with pyrite.

Part Two: Experimental Observations

Experimental Methods

Small 3cm x 1.5cm x 1.5cm blocks weighing between 7g and 11g were cut from the seven highway cores examined in the first section of this report. Two blocks from each core were immersed in 100 ml of solution and sealed in cleaned polymethylpentene containers that were stored for 132 hours at 58°C in a constant temperature chamber. The solutions used were 0.75 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, CMA based on a molar ratio of 3:7, i.e. $3[\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}] : 7[\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, Na_2SO_4 , $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and distilled water. All solutions contained 0.01% sodium azide to control bacterial growth. Two types of experiments were performed. Wet/Dry Cycling: After being immersed in 58°C solutions for 132 hours, blocks were removed from the solutions, dried 58°C (°135°F) for 24 hours, air cooled to 25°C, returned to their immersion solutions at 25°C, and again stored at 58°C for 132 hours. Freeze/thaw cycling: Samples removed from the 58°C solutions after 132 hours were air cooled to 25°C and stored for 24 hours in a freezer at -4°C (25°F). The blocks were air warmed to 25°C, returned to their respective solutions at 25°C, and stored at 58°C for 132 hours. Both types of experiments were continued until the blocks exhibited cracking or crumbling, at which time they were rinsed, dried, and prepared for petrographic and SEM analysis. These experiments were similar to those reported by Cody et al. (1996) but the current experiments used less concentrated solutions in order to more closely simulate road conditions where deicers may be applied, and expanded the previous study to include acetates and Na sulfate.

Relative Aggressiveness of Salt Solutions

General conclusions about the effects of these experiments are as follows.

Acetates. Calcium magnesium acetate solutions were the most damaging of all solutions tested. Wet/dry and freeze/thaw cycling in CaMg-acetate produced widespread and severe damage with cracking from replacement of calcium silicate hydrate with non-cementitious magnesium silicate hydrate. Brucite formation was extremely copious, and it was disseminated throughout the cement paste and in voids. It also occurred at the paste-fine aggregate interface where it caused debonding of fine aggregate. Mg-acetate produced similar but slightly less damage, and Ca-acetate solutions produced much less alteration. CaMg-acetate dissolved the cement paste and altered quartz fine aggregate but it is still not clear why it is more deleterious than Mg-chloride or Mg-acetate. We should point out that we mixed our own CaMg-acetate and did not use a commercial variety; commercial formulations of CMA may not have the same aggressiveness to concrete as our mixture of calcium acetate and magnesium acetate.

Sulfates. Sodium sulfate solutions were next to CaMg-acetate and Mg-acetate in aggressiveness. Both wet/dry and freeze/thaw cycling in these solutions produced severe expansion cracking, with wet/dry conditions being worse. Sulfate solutions applied to Sundheim concrete that previously did not contain ettringite pro-

duced abundant ettringite disseminated throughout the paste and in voids, and cracking resulted. Deterioration by ettringite expansion is clearly evidenced by these experiments.

Chlorides. Magnesium chloride produced significant concrete crumbling because of widespread replacement of CSH by non-cementitious MSH. Our research results show that calcium chloride deicing salts caused characteristic deterioration in concretes with reactive dolomite aggregates by enhancing dedolomitization that releases magnesium to form destructive brucite and MSH. Sodium chloride solutions did not cause significant changes except that chloride causes the formation of chloroaluminate, probably trichloroaluminate produced from pre-existing ettringite.

Magnesium. In our experiments, the magnesium component of deicer salts proved to be the most deleterious. Magnesium promoted replacement of CSH by non-cementitious MSH with resultant paste shrinkage and cracking. The growth of abundant, potentially-expansive brucite especially in the paste-fine aggregate interface furthered debonding of fine aggregate.

CONCLUSIONS

Our studies of Iowa highway concrete deterioration strongly support the contention that expansive mineral growth is at least partly responsible for premature deterioration. The evidence concerning brucite expansion is, however, not conclusive. In spite of numerous studies that have concluded brucite growth is expansive (6), we found no evidence for microcracking directly associated with brucite crystal occurrences. The only supporting data is that analysis of brucite precipitation reactions (6) shows that there is a theoretical expansion when cement and dolomite components react to produce brucite. It is also observed that brucite is most common in poorly-performing concretes that exhibit expansion phenomena such as D-cracking.

Our evidence that ettringite creates expansion cracking is stronger than that for brucite. The exact mechanism of cracking is uncertain, but we conclude that abundance of delayed ettringite growth in poorly-performing concretes and the close association with microcracks is good evidence for ettringite growth induced deterioration. This conclusion is supported by experiments showing that abundant cracks accompanied newly-formed ettringite.

Experiments with different potential deicers and Na-sulfate document that all of these chemicals cause concrete deterioration. Magnesium solutions are especially damaging, and consequently support our conclusion that magnesium released from dolomite coarse aggregate decreases service life of concretes. The enhanced damage by calcium magnesium acetate was unexpected and suggests that the effects of CMA on highway concretes should be closely monitored over a prolonged period to determine if similar effects develop over long-term use.

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Lee et al.

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