PCC Highway Deterioration by Growth of Expansive Minerals induced by Alkali-Aggregate Reactions.

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1. INTRODUCTION

Considerable progress has been made in reducing premature failure of highway concrete, but several problem areas remain. A highly significant problem is the importance of expansion resulting from newly-formed minerals in concrete. New minerals form over time in concrete as a result of various chemical reactions involving cement paste and coarse/fine aggregate that are grouped into a general category termed "alkali-aggregate reaction (AAR)". Although many Iowa concrete highways are in good condition after 40 years of heavy road use, some highways show severe deterioration after only 8-10 years. Two important secondary minerals, brucite ($Mg(OH)_2$) and ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ or $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), are often implicated in premature deterioration, and the cause of deterioration is often attributed to expansion and cracking related to their growth. The present study investigates the role that these and other potentially expansive minerals have in premature deterioration of Iowa highway concretes.

2. METHODS OF STUDY

Ten core samples with different aggregate sources and different service records were obtained from seven different Iowa highways by personnel of the Iowa Department of Transportation (Table I). Selection of the core samples was on the basis of premature

deterioration of the highways which Iowa DOT personnel believed probably was due to adverse reactions between coarse aggregate and cement paste.

Each of the four-inch diameter concrete highway cores obtained from the Iowa DOT were cut into small rectangular blocks, approximately 2cm x 2cm x 4cm. Polished thin-sections were made from blocks from the top (1" from top of the road surface) and bottom (1" 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. Petrographic examination was 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.

A Hitachi S 2460 reduced-vacuum scanning electron microscope was used in this study. Back-scattered images 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.

3. RESULTS AND DISCUSSIONS

### General Characteristics of Iowa highway concrete Samples

The highly alkaline environment (pH 11-12) of Portland cement induces reactions between coarse/fine aggregate particles of concrete and the Portland cement paste, and these reactions are grouped into a general category termed "alkali-aggregate reaction (AAR)". Three major types of these alkali-aggregate reactions have been reported (Gillott 1975; Tang 1992; Rogers 1993; West 1996): (1) alkali-carbonate reaction (ACR), (2) alkali-silica

reaction (ASR), and (3) alkali-silicate reaction. Among these reactions, ACR is the most significant for Iowa highway concretes because carbonate rocks are chiefly used in their construction (Lemish et al. 1958; Cody et al. 1994). The alkali-carbonate reaction is characterized by dedolomitization of dolomitic limestones, calcitic dolostone, and dolostone (Gillott and Swenson 1969). The majority of core samples were concretes with dolomite coarse aggregate. Previous research (Cody et al., 1994) divided them two groups, durable and non-durable concretes, based on their service records. 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 (Table1) is classified as durable; all others were non-durable. These terms have no necessary correspondence with ASTM-defined durability. Durability correlates with dolomite coarse aggregate reactivity. Poorly performing concretes contain fine grained, poorly-crystallized, micro-porous dolomite that has reacted with surrounding concrete paste to produce dark and light-colored partially-dedolomitized rims surrounding the dolomite aggregate fragments.

Newly Formed Minerals in Iowa Highway Concrete

Abundant brucite and ettringite were commonly occurred in non-durable highway concretes studied, and were the only potentially expansive substances identified by petrographic microscope and electron imaging methods.

Brucite: In Iowa highway concrete (i.e., non-durable concrete) containing reactive dolomite coarse aggregate, abundant brucite and calcite formed via dedolomitization reaction:

$$CaMg(CO_3)_2 + 2\,MOH = CaCO_3 + Mg(OH)_2 + M_2CO_3 \qquad (1)$$
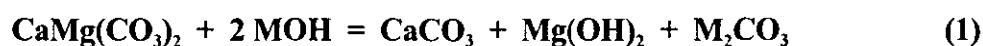
where M represents alkali substances (mainly Na or K).

The alkali carbonate produced by reaction (1) reacts with portlandite, $Ca(OH)_2$ of the Portland cement and regenerates alkali:

$$M_2CO_3 + Ca(OH)_2 = 2\,MOH + CaCO_3 \qquad\qquad (2)$$

The cement paste of many non-durable concrete samples frequently contains comparatively large (< 10 um) brucite masses or nodules (Fig. 1), whereas brucite in dolomite coarse aggregate is characterized by extremely small (< 1 um), disseminated masses that are visible as small white spots in Mg-O element maps. The very small size and widespread dissemination indicate that most of the brucite in dolomite aggregate interiors may exist as microcrystalline material associated with newly-formed microcrystalline calcite that has grown on the surface of preexisting dolomite crystals. Larger, spherical to irregular shaped brucite masses are also disseminated in the unaltered cement paste far from dolomite aggregate particles. This factor 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 relation with cracks in cement or coarse aggregate.

Etrringite: 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 (Fig. 2). It occurs in two forms in these air-entrainment voids. The first type is void-fill ettringite 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. The two types of ettringite depend on a relation between the amount of ettringite-forming pore solutions and the size of void spaces. The vast majority of ettringite crystals occur in air-entrainment voids, but minor amounts of ettringite also fill microscopic interstitial pores in the cement paste. Interstitial cement pore space filled by ettringite was observed in high magnification back-scattered SEM images. Rarely, ettringite also occurred in pre-existing cracks. Under high-magnification, detailed observations of paste micro-cracks that extend from ettringite-filled voids reveal that ettringite does not occur in them. This observation provides strong evidence that the micro-cracks developed after ettringite formation.

Relationship of Ettringite to Pyrite Inclusions

Sulfate (SO^{2-}_4) 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 (Oberste-Padtburg et al. 1984; Casanova and Aguado 1996). Ettringite typically occurs in the cement paste near dolomite aggregates that contain pyrite inclusions and ettringite abundance is closely related to the amount of pyrite oxidation as evidenced by the quantities of goethite and/or ferrihydrite associated with the pyrite. Oxidation of pyrite is affected by dolomite coarse aggregate properties and by the location of pyrite in these aggregates. Crystal size, the degree of crystallinity and porosity, and aggregate reactivity affect pyrite oxidation. Pyrite inclusions in reactive dolomite aggregate are more oxidized than those in non-reactive dolomite aggregate because of fine crystalline sizes and greater micro porosity in the reactive dolomite aggregate that allow oxidizing solution to react with pyrite .

4. CONCLUSIONS

The present studies of highway concrete deterioration strongly support the contention that expansive mineral growth is at least partly responsible for premature deterioration. Ettringite was most common in poorly performing concretes. Ettringite completely filled many small voids and occurred as rims lining the margins of large voids. Severe cracking of cement paste was often closely associated with the secondary ettringite. Some ettringite was present as microscopic crystals in the cement paste. Micro-cracks originated from ettringite location and propagate into the cement paste. Pyrite is commonly present as inclusions in coarse/fine aggregates, and its oxidation products were present in many concrete samples. Sulfate ions (SO_4^{2-}) derived from pyrite oxidation contributed to ettringite formation. The oxidation of pyrite in aggregate particles was affected by several factors such as aggregate type, aggregate reactivity, and pyrite size and location. Most brucite is microscopic in size although a few crystal masses are larger. No expansion cracks are spatially associated with brucite deposits but this is not conclusive evidence against brucite-induced expansion. Brucite is widely disseminated so that expansion at innumerable micro-locations may cause general concrete expansion which should be relieved by cracking (D-cracking) at weaker locations in the concretes.

As a broad generalization, it can be concluded from this research that reactive dolomite aggregate, especially that containing pyrite, is highly deleterious to concrete durability. Dedolomitization of reactive aggregate leads to a variety of problems including formation of secondary minerals such as calcite and brucite, and possible formation of magnesium silicate hydrate as a result of Mg release to pore solutions. Coarse and fine aggregate with pyrite inclusions are harmful because pyrite oxidation produces sulfate that reacts with C_3A to produce ettringite. The most easily oxidized pyrite masses are those

exposed to oxidizing solutions by being located adjacent to abundant micropores and intercrystalline channels that most commonly occur in reactive types of coarse aggregate.

5. REFERENCES

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Table 1. Concrete core locations and other data for Iowa highway concretes.

| Sample No.	Core Location	Year*	Coarse Aggregate Source	Portland Cement
A	I-35, Cerro Gordo Co.	1974	Portland West quarry, Shellock Fm.	Northwestern I
B	US 30, Linn Co.	1981	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Lehigh I
C	IA 9, Howard Co.	1974	Dotzler quarry, Spillville Fm.	Lehigh I
D	IA 21, Iowa Co.	1982	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Martin Marietta (?)
E	US 63, Howard Co.	1971	Nelson quarry, Cedar Valley Fm.	Dewey I
F	US 20, Dubuque Co.	1988	Sundheim quarry, Hopkinton Fm	Davenport I
G	IA 100, Linn Co.	1989	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Continental III
Gan-1	US 63, Tama Co.	1972	Smith quarry, Coralville Member, Cedar Valley Fm.	Lehigh I
Gan-2	US 151, Linn Co.	1947	Paralta quarry, Otis Member, Wapsipinicon Fm.	Mixed (Medusa, Lehigh, Dewey, Atlas, Alpha)
Gan-3	US 218, Benton Co.	1971	Garrison quarry, Coralville Member, Cedar Valley Fm.	Davenport I

* Year: the highway was constructed.
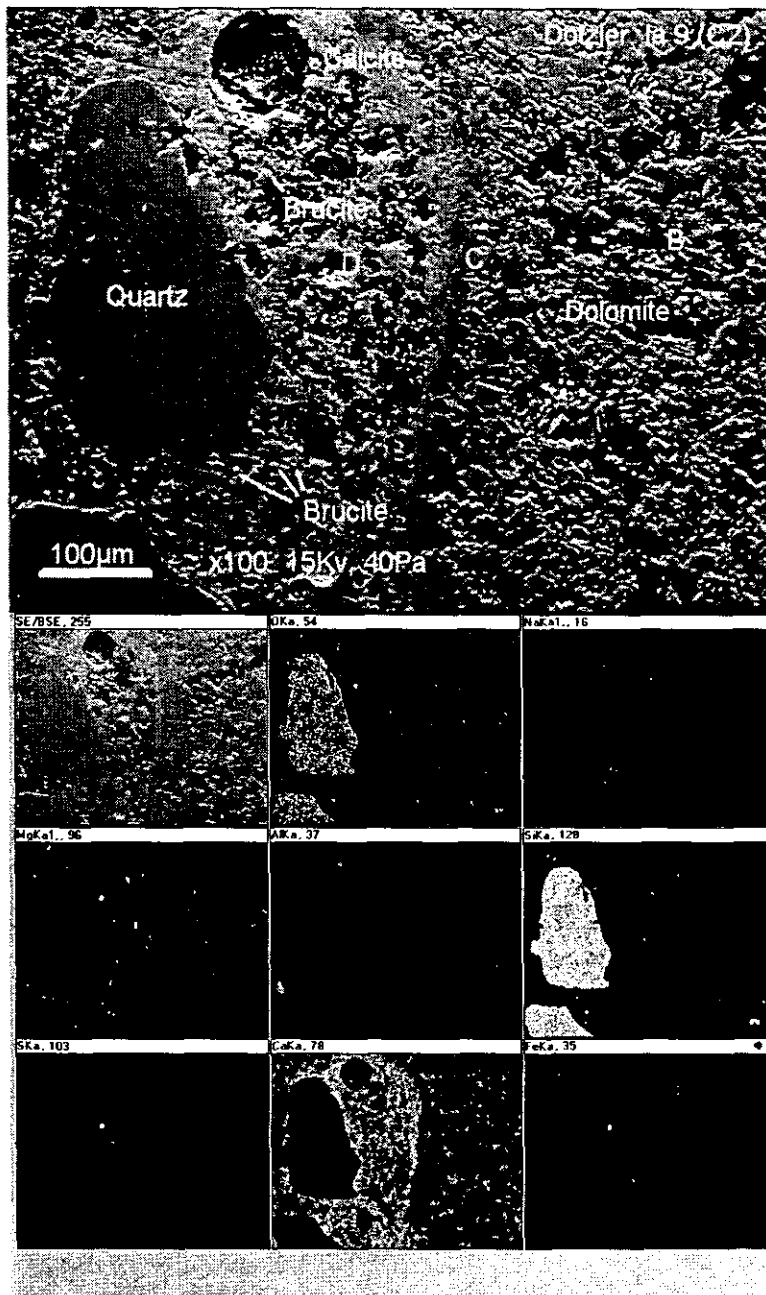
Fig. 1. SEM micrograph and EDAX maps of same area showing brucite occurrence and calcite enrichment in dolomite coarse aggregate and cement paste. Note the calcite enrichment in the outer rim of the coarse aggregate fragment in the Ca-map, and the brucite occurrence as shown by small white area and dots in Mg-map. Dotzler quarry aggregate (IA 9).
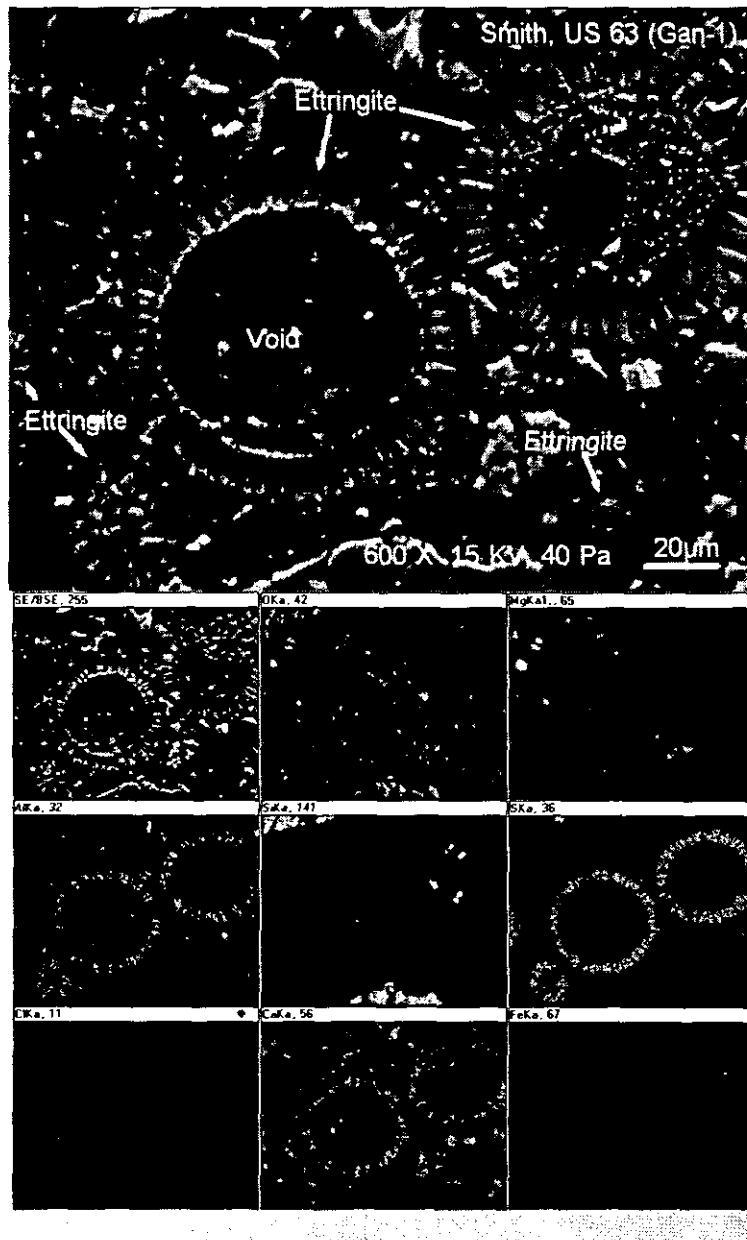
Fig. 2. SEM micrograph and EDAX maps showing both void-rim and void-fill types of ettringite in cement paste. Void-rim ettringite occurs as a rim that lines the margin of air entrainment voids (>100 µm) in the cement paste. Radial cracks are well developed in this type of ettringite. Void-fill ettringite occurs in small air-entrainment voids (< 100 µm), and microcracks propagate out into cement from them.