

## 콘크리트 포장 도로의 성능저하에 관련된 이차광물형성과 팽창메카니즘

### Secondary Mineral Formation and Expansion Mechanisms Involved in Concrete Pavement Deterioration

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#### 요약/Abstract

새로이 형성되는 이차광물들이 콘크리트의 조기 성능 저하 (열화)에 미치는 영향은 현재까지 명확히 규명되지 않고 있다. 이들 광물들은 시멘트 페이스트와 골재간의 화학적 반응의 결과로 시멘트 페이스트 내에 형성된다. 조기 성능 저하 현상을 보이는 미국 아이오와주의 콘크리트 포장의 고속도로들로부터 채취된 시료들 내의 골재와 시멘트 페이스트에서의 화학적 광물학적 변화를 규명하기 위하여 암석학적 관찰과 SEM/EDAX 분석을 실시하였다. 이러한 분석에 의거 성능 저하에 연관된 이차광물의 형성과 팽창 메카니즘에 대하여 연구하였다.

브루사이트(Brucite,  $Mg(OH)_2$ )는 골재의 탈백운석화 (dedolomitization) 반응의 결과로 시멘트 페이스트 내에 생성되는 잠재적인 팽창성 광물이다. 시멘트 페이스트의 균열현상은 이들 광물과 공간적인 연관성을 보여주지는 않으나, 대부분이 극 미세입자의 크기로 조기 성능 저하 현상을 나타내는 콘크리트의 시멘트 페이스트 내에 광범위하게 산재되어 나타난다. 무수한 미세공간들에서의 이들 광물 성장에 의한 팽창성 응력은 콘크리트내부의 약한 부분에서 균열로 나타난다.

에트린자이트 ( $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ )는 많은 작은 공극들을 완전히 채우고 있으며, 큰 공극들의 가장자리에 테두리와 같은 형태로 나타난다. 미세한 에트린자이트가 많은 콘크리트 시료들의 시멘트 페이스트에 산재해서 나타나기도 한다. 조기 성능 저하의 원인이 되는 시멘트 페이스트의 심한 균열이 에트린자이트와 공간적으로 연관되어 나타나는데, 이러한 사실은 에트린자이트가 콘크리트의 성능 저하에 기여한다는 것을 지지한다. 황철석 ( $FeS_2$ )이 일반적으로 골재 내에 산재하는데, 이 광물의 산화작용의 산물이 많은 콘크리트 시료들에서 관찰된다. 이런 황철석의 산화작용은 에트린자이트를 형성하기 위한 황산염을 공급하게 된다.

A significant question is what role does newly-formed expansive mineral growth play in the premature deterioration of concrete. These minerals formed in cement paste as a result of chemical reactions involving cement paste and coarse/fine aggregate. Petrographic observations and SEM/EDAX analysis were conducted in order to determine chemical and mineralogical changes in the aggregate and cement paste of samples taken from Iowa concrete highways that showed premature deterioration. Formation and expansive mechanisms involved in deterioration were investigated.

Brucite,  $Mg(OH)_2$ , is potentially expansive mineral that forms in cement paste of concretes containing reactive dolomite aggregate as a result of partial dedolomitization of the aggregate. No cracking was observed to be spatially associated with brucite, but most brucite was microscopic in size and widely disseminated in the cement paste of less durable concretes. Expansion stresses associated with its growth at innumerable microlocations may be relieved by cracking at weaker locations in the concrete.

Ettringite,  $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ , completely fills many small voids and occurs as rims lining the margin of larger voids. Microscopic ettringite is common disseminated throughout the paste in many samples. Severe cracking of cement paste causing premature deterioration is often closely associated with ettringite locations, and strongly suggests that ettringite contributed to deterioration. Pyrite,  $FeS_2$ , is commonly present in coarse/fine aggregates, and its oxidation products is observed in many concrete samples. Pyrite oxidation provides sulfate ions for ettringite formation.

**Key word:** Deterioration, Concrete, Dedolomitization, Brucite, Ettringite,

## INTRODUCTION

Concrete containing certain types of aggregates has a poorer service record than many very old concrete, and this problem has been noted as a pervasive problem through the United States and other countries. Iowa highways in U.S. constructed of concrete containing carbonate rock coarse aggregate from certain quarries sometimes have service lives of less than 10 years (Cody et al., 1994). New minerals form in cement paste as a result of chemical reactions involving cement paste and coarse/fine aggregate. A highly significant problem is the importance of expansion resulting from newly-formed minerals in concrete. 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. Brucite precipitation in concrete produced by magnesium released from the dolomite coarse aggregate and/or from other sources may be a cause of reduced concrete service life, but the specific mechanisms and the importance of expansion in the deterioration of concrete by brucite growth are still controversial. The other potentially important deleterious mineral is ettringite. Ettringite formed long after concrete has hardened referred to as delayed ettringite. The formation of delayed ettringite is widely believed to cause expansion of concrete, but the

mechanism involving expansion remains controversial. Delayed ettringite formation is especially enhanced by the availability of sulfate.

This study investigates the role that these and other potentially expansive minerals have in premature deterioration of concrete pavements.

## METHODS OF STUDY

### Collection of Highway Concrete Samples

Ten core samples with different aggregate sources and different service records were obtained from nine different Iowa highways by personnel of the Iowa Department of Transportation (Table 1). Selection of the

core samples was on the basis of premature deterioration of the highways which Iowa DOT (Department of Transportation) personnel believed probably was due to adverse reactions between coarse aggregate and cement paste. Coarse aggregates used in these concretes were from Portland West, Crawford-Lee, Dotzler, Nelson, Smith, Paralta, Garrison and Sundheim quarries. Concrete containing Sundheim coarse aggregate was included as an example of concretes containing high performance aggregate.

### General Procedures and Instrumentation

Each of the four inch diameter concrete

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

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

## CHARACTERISTICS OF IOWA HIGHWAY CONCRETE SAMPLES

### Durable and Non-Durable Concretes

The majority of core samples were concretes constructed with dolomite coarse aggregate. Previous research (Cody et al., 1994) classified these Iowa highway concretes into two groups, durable and non-durable, based on their service records (table 1). The term "durable concrete" was used for the highway concretes containing coarse aggregate from Sundheim quarry that had extended service lives of > 40 years before significant deterioration had

Table 2. Chemical composition of dolomite aggregate.

Aggregate Source	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	S	FeO*	TiO <sub>2</sub>	CO <sub>3</sub>	Total
Portland West	16.47	32.58	4.40	1.11	0.56	0.01	0.02	0.30	0.44	0.06	43.52	99.49
Crawford, Lee	18.47	32.88	0.82	0.15	0.05	0.01	0.04	0.34	0.51	0.01	45.94	99.23
Nelson	17.00	33.97	2.19	0.04	0.18	0.02	0.02	0.26	0.33	0.02	45.19	99.57
Dotzler	20.30	29.67	2.69	0.59	0.25	0.03	0.01	0.30	0.27	0.04	45.42	99.57
Sundheim	20.11	30.41	2.56	0.49	0.20	0.01	0.02	0.03	0.15	0.03	45.82	99.84
Smith	18.24	32.71	1.74	0.40	0.14	0.02	0.00	0.35	0.34	0.02	45.59	99.56
Paralta	22.01	29.47	0.59	0.11	0.06	0.01	0.03	0.04	0.23	0.01	47.15	99.72
Garrison	18.38	32.13	1.57	0.36	0.13	0.01	0.03	0.66	0.62	0.01	45.28	99.19

occurred. "Non-durable concrete" was used for highway concretes which had service lives of <16 years according to service records in Iowa DOT. The highway concrete containing Sundheim aggregate that shows good service records can be classified as durable; all others were non-durable. These terms have no necessary correspondence with ASTM-defined durability.

#### Dolomite Coarse Aggregate Characteristics

Durability correlates with dolomite coarse aggregate reactivity. Reactive dolomite aggregate consists of mostly fine-grained (<75  $\mu$ m), poorly-formed dolomite crystals with many small void spaces between the loosely intergrown crystals. Non-reactive dolomite aggregate typically consists of coarse-grained (>75  $\mu$ m), well-formed dolomite crystals that are tightly intergrown and contain few voids. Reactive dolomite coarse aggregates are characterized by dedolomitization reaction rims, which are shown in Figure 1. Five dedolomitized reaction zones at the dolomite-paste interface were identified: an unaltered dolomite aggregate interior (not seen in figure), two reaction rims on the margin of dolomite aggregate (an inner dark dolomite rim, Zone B, and an outer light-colored dolomite rim, Zone C), a light-colored paste rim (Zone D), and unaltered cement (outside of zone D). In this paper, we will follow this usage. The presence and/or thickness of these rims and the spatial distribution of the zones are related to the aggregate reactivity and are not always identical within different parts of the same concrete sample.

Bulk chemical analyses show that the dolomite aggregates in durable and non-durable concretes do not show significant differences in chemical composition (Table 2). All the dolomite aggregates contain approximately

20 wt. % MgO and 30 wt. % CaO, which is close to the theoretical composition of dolomite, 21.86 wt. % MgO and 30.41 wt. % CaO. Positive correlations among SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O indicate the presence of small amounts of clay minerals as impurities.

#### Fine Aggregate Characteristics

About 25 to 35 vol. % of the concrete consists of fine aggregate (< 2.5 mm diameter) that consists chiefly of quartz, with minor amounts of orthoclase feldspar, clay minerals, ferromagnesian minerals such as biotite and amphibole, goethite, and limonite.

Quartz is present as discrete detrital grains, although it also occurs as fragments of quartz-bearing rocks. Detrital quartz is rounded to sub-angular. Strained quartz, indicated by undulatory extinction, is often present. This type of quartz is reactive and is often involved in alkali-silica reactions, which produce expansive silica gel responsible for cracking of quartz grains and/or cement paste (Smith et al., 1992; Grattan-Bellow, 1992).

Petrographic observation of thin-sections shows that quartz grains in most samples are generally unaltered from their original state, but some grains have undergone cracking. Microcracks occur in the paste adjacent to a few of the strained quartz grains. These cracks may be caused by expansion resulting from the alkali-silica reaction, but there is little evidence of much silica gel adjacent to strained quartz grains.

Other silicate minerals are predominately feldspars that include plagioclase, orthoclase, and microcline. Potassium- and sodium-rich clay minerals are also present and minor cracking of aggregate and paste is observed next to them.

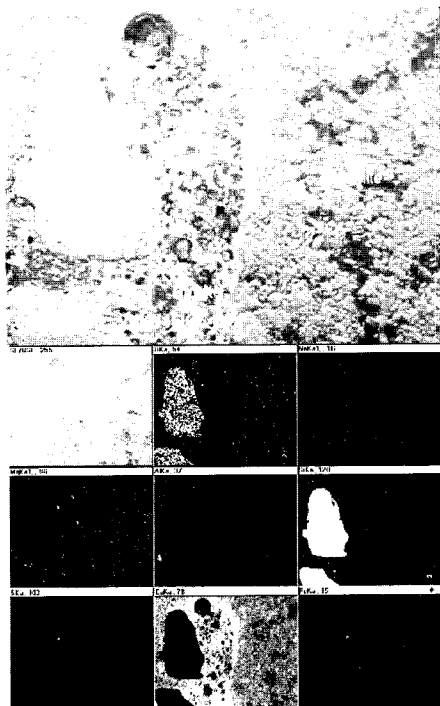


Fig. 1. SEM micrograph and EDAX maps of same area showing brucite occurrence and calcite enrichment in dolomite coarse aggregate and cement paste. Note the calcite enrichment in the outer rim of the coarse aggregate fragment in the Ca-map, and the brucite occurrence as shown by small white area and dots in Mg-map. Dotzler quarry aggregate (IA 9). Note that B, C, D are dedolomitization reaction rims: zone B = an inner dark dolomite rim, zone C = an outer light-colored dolomite rim, and zone D = a light colored paste rim.

### Cement Paste Characteristics

#### *Chemical Composition of Cement Paste*

Five different types of Portland cement were used in the construction of the Iowa highway concretes (Table 1). All of the cements are type I, except for one type III used in the construction of IA 100. Bulk chemical analyses of the cements were obtained by the Iowa DOT, and the average, standard deviation, maximum and minimum values of duplicate

analyses are listed in Table 3. In this table, Potential Compound Composition refers to the maximum compound composition allowable by ASTM C150. The MgO content of concrete should be limited to 4~5 wt. % because an excess causes formation of the mineral periclase (MgO) that may expand by a slow hydration reaction to brucite which may cause concrete damage (Taylor, 1990). The content of MgO in the Portland cement varies from 2.35 to 3.38 wt. %, which is within ASTM suggested limits (Table 3). The amount of SO<sub>3</sub> should be limited to between 2.5 and 4 wt. %, because an excess of SO<sub>3</sub> can cause expansion by the formation of delayed ettringite (Taylor, 1990). The SO<sub>3</sub> content of the Portland cements (Table 3) is within this limit. Type I cement contains 2.71 % to 3.16 wt. % whereas type III cement has a somewhat higher content of 3.57 wt. % SO<sub>3</sub>. Alkalis (K<sub>2</sub>O and Na<sub>2</sub>O) are also important constituents of Portland cement because they can create deleterious alkali aggregate reactions. Alkali contents should be < 0.6 wt. % Na<sub>2</sub>O (Na<sub>2</sub>O equivalent = Na<sub>2</sub>O + K<sub>2</sub>O), and Na<sub>2</sub>O equivalents of the studied cements listed are within this limit except for the Davenport (type I), which is slightly over the limit (0.66 % equivalent Na<sub>2</sub>O).

#### *Air-Entrainment Voids*

The concretes studied here contain very similar amounts of entrained air ( $6 \pm 1 \frac{1}{2}$  vol. %). Air-entrainment voids appear to be uniformly distributed, are spherical in shape, and void diameters vary from several tens of microns to several millimeters. Sample F (US 20) and G (IA 100) contain tiny spherical grains of class C fly ash.

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Table 3. Composition of portland cement used for Iowa highway concretes.

Name of Portland Cement		Chemical Composition, %						Na <sub>2</sub> O equiv.	Loss of Ignition, %	Insoluble Residue, %	Total	Potential Compound Composition, %			
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>					C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
Davenport (Type I)	Avg.	21.22	4.50	2.81	63.23	3.17	2.71	0.66	1.03	0.29	99.87	54.22	19.92	7.15	8.56
	stddev.	1.23	0.39	0.39	1.17	0.50	0.24	0.12	0.31	0.20					
	Max.	24.76	6.65	4.14	65.45	4.65	3.4	0.94	2.07	1.28					
	Min.	17.09	2.92	2.16	55.1	1.57	1.97	0.37	0.44	0.02					
Continental (Type I)	Avg.	21.24	4.75	2.24	63.95	3.40	2.94	0.33	1.37	0.21	100.54	55.47	19.05	8.78	8.83
	stdv.	1.15	0.62	0.53	1.10	0.67	0.34	0.21	3.53	0.16					
	Max.	24.24	6.14	3.39	67.61	5.12	4.23	0.83	3.01	0.92					
	Min.	19.07	2.58	1.3	61.34	2.01	2.44	0.01	0.44	0.00					
Continental III (Type III)	Avg.	20.67	4.98	1.37	63.96	3.38	3.57	0.09	1.27	0.23	99.52	57.73	15.70	10.87	4.17
	stddev.	0.33	0.14	0.01	0.36	0.17	0.17	0.02	0.11	0.10					
	Max.	20.94	5.14	1.39	64.30	3.52	3.71	0.12	1.38	0.35					
	Min.	20.27	4.82	1.36	63.47	3.14	3.33	0.07	1.13	0.12					
Lehigh (Type I)	Avg.	21.19	4.95	2.36	63.89	2.62	3.16	0.56	0.98	0.29	100.23	53.45	20.43	9.12	7.17
	stddev.	1.36	0.36	0.21	1.39	0.55	0.23	0.12	0.35	0.36					
	Max.	25.57	6.09	3.37	67.18	4.72	3.78	0.82	1.81	2.66					
	Min.	18.05	3.36	2.03	60.37	0.95	2.22	0.40	0.17	0.03					
Northwestern (Type I)	Avg.	21.65	4.94	2.04	64.11	2.35	2.97	0.47	1.06	0.26	100.02	51.89	22.93	9.62	6.21
	stddev.	1.59	0.31	0.46	1.15	0.71	0.28	0.14	0.33	0.13					
	Max.	24.53	5.51	3.1	67.44	4.22	3.67	0.81	2.15	0.69					
	Min.	18.68	3.78	1.55	62.05	1.15	2.05	0.21	0.4	0.03					
Martin Marietta*		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Dewey I*		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

\* Chemical composition data was not available from DOT

## RESULTS AND DISCUSSION

### EXPANSIVE MINERALS FEATURES OF IOWA HIGHWAY CONCRETES

Abundant brucite and ettringite were observed in most of the highway concretes studied, and large amounts of calcite mineralization occurred at dedolomitization reaction rims at interface between dolomite aggregate and cement paste (Fig.1). These minerals were the only potentially expansive substances identified by petrographic microscope and electron imaging methods. Gypsum was not detected in significant amounts in any samples.

#### Brucite, $Mg(OH)_2$

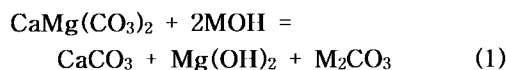
##### *Forms and distribution*

The cement paste of many non-durable concrete samples frequently contains comparatively large ( $< 10 \mu m$ ) brucite masses or nodules (Fig. 1), whereas brucite in dolomite coarse aggregate is characterized by extremely small ( $< 1 \mu m$ ), 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 exists 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 paste or coarse aggregate.

#### *Brucite Formation Reactions*

The greater abundance of brucite,  $Mg(OH)_2$ , in Iowa concretes containing reactive dolomite aggregates than in those with non-reactive dolomite is strong evidence that brucite is a by-product of the release of magnesium ions by dedolomitization of dolomite,  $CaMg(CO_3)_2$ :



where M represents alkali substances (mainly Na or K).

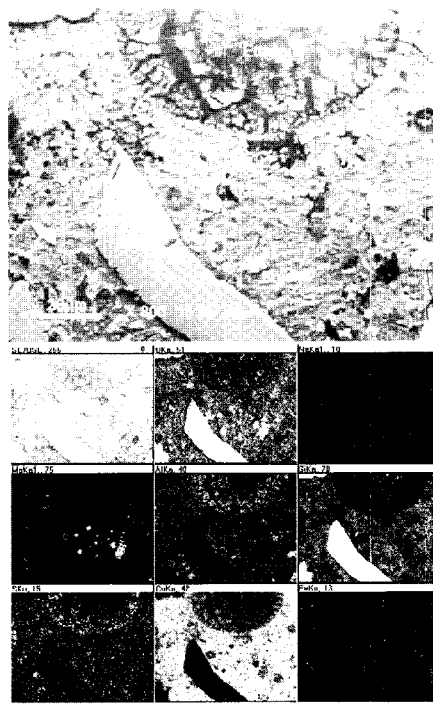
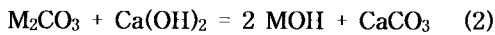


Fig. 2. SEM micrograph and EDAX maps showing the brucite and ettringite formation in the unaltered cement paste. Small brucite crystals,  $< 20 \mu m$  size, occur in irregular shaped nodules in the cement matrix. Note that open spaces are developed in

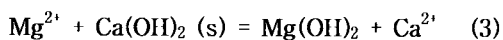


the vicinity of brucite. Ettringite completely fills the large air-entrainment voids and interstitial pores in the cement paste. Cracks developed in ettringite and extend into the paste, and probably were caused by ettringite expansion or ice expansion in ettringite-clogged voids. Very small ettringite deposits also occur in the cement matrix.

In concrete, the alkali carbonate produced by reaction (1) reacts with portlandite,  $\text{Ca(OH)}_2$ , in Portland cement and regenerates alkalis :



Examination of EDAX area maps of many samples indicates that brucite growth in dedolomitization reaction zones are much less than calcite and more brucite forms in unaltered cement paste. In fresh portion of cement paste, more brucite formed by topochemical reactions between magnesium ions and portlandite in the cement matrix rather than by direct precipitation in void because the common irregular-shaped nodular brucite has no clear relationship to pre-existing voids in cement paste (Fig. 2). This topochemical reaction can be written as follow:



This would also explain the lack of brucite in altered cement paste. In this reaction zone, topochemical reactions between dissolved magnesium and hydroxyl ions on portlandite surfaces is limited because portlandite is depleted during its transformation to calcite via alkali-dolomite reaction. According to Cohen (1983), a topochemical reaction is defined as "a reaction between a solid particle and a surrounding solution in which the hydration product is formed on the surface of the particle."

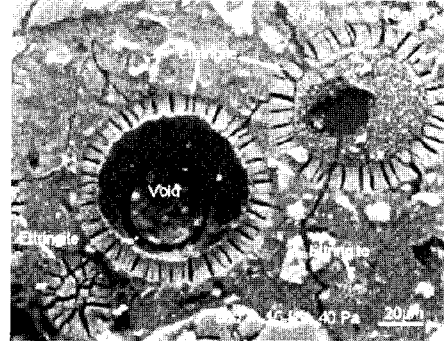


Fig. 3. SEM micrograph showing both void-rim and void-fill types of ettringite in cement paste. Void-rim ettringite occurs as a rim that lines the margin of air entrainment voids (>100 μm) in the cement paste. Radial cracks are well-developed in this type of ettringite. Void-fill ettringite occurs in small air-entrainment voids (< 100 μm), and microcracks propagate out into cement from them.

**Ettringite,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$   
or  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}26\text{H}_2\text{O}$**

#### *Forms and Distribution*

In 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 (Fig. 3). The first type is void-fill ettringite in which the mineral completely fills small air-entrainment voids (diameter less than about 100 μm). The second type is void-rim ettringite that occurs as rims of ettringite lining the margin of large voids (diameter greater than about 100 μm). 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 (Fig. 3). It also filled narrow cracks along margins of fine aggregate particles (Fig. 4). These cracks formed along the boundary between quartz fine aggregate particles and

cement paste, and appear to result from alkali-silica reaction-induced expansion. Severe cracking of cement paste causing premature deterioration is often closely associated with ettringite locations. Under high-magnification, detailed observations of paste micro-cracks that extend from ettringite-filled voids reveal that ettringite does not occur in them (Fig. 2, 3). This observation provides strong evidence that the micro-cracks developed after ettringite formation.

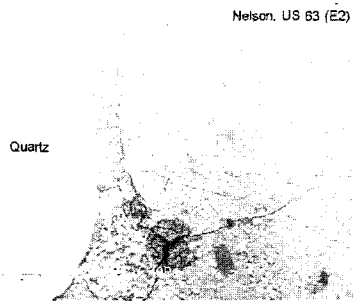


Fig. 4. SEM micrograph showing ettringite in pre-existing cracks. Ettringite forms along the pre-existing cracks between quartz aggregate and cement paste. The cracks appear to be formed by expansive alkali-aggregate reaction. Microcracks extend from ettringite into the cement paste.

#### ***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 (Oberholster 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 (Fig.5). The

oxidation of pyrite is affected by carbonate coarse aggregate properties and by the location of pyrite in these aggregates. Crystal size, the degree of crystallinity and porosity, and aggregate reactivity are important in affecting 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 reactive dolomite aggregate that allows oxidizing solution to react with pyrite. This fact suggests that sulfate ions released by pyrite oxidation significantly contributed to ettringite formation. The maximum sulfate contributed by the oxidation of pyrite in dolomite coarse aggregate can be roughly estimated from the sulfur content in the aggregate and the mixing specifications for concrete under the following assumptions: (1) all sulfur in coarse aggregate exists as pyrite, (2) all pyrite inclusions are oxidized, (3) the average mixing specification (coarse aggregate is 40 wt. % of total concrete; fine aggregate is 40 wt. %; the water/cement ratio is 0.45), and (4) all pyritic  $\text{SO}_4^{2-}$  migrates from aggregate into the cement. Calculations show that 0.3 wt. % of sulfur content in the coarse dolomite aggregate can result in the addition of up to 2.61 wt. % of  $\text{SO}_3$  in cement paste.

#### ***Other Potential Sulfate Sources***

Petrographic observations indicate that much ettringite is rather uniformly disseminated through cement pastes of the older highways studied here (I 35, IA 9, US 63, US 151 and US 218). Some of this ettringite may result from long-term deicer applications on these older highways. According to Pitt et al. (1987), rock salt (NaCl) applied as a deicer on Iowa highways contains up to 4 wt. % sulfate impurities such as gypsum and magnesium sulfate. These minerals dissolve and their

ions migrate downward into the concrete where they may react with tricalcium aluminate (C<sub>3</sub>A) in the paste to form ettringite. Deicer sulfate impurities probably significantly contributed to the formation of ettringite in Iowa highway concretes. For highway concrete, other potential sulfate sources are sulfur dioxide from the combustion of motor fuels.

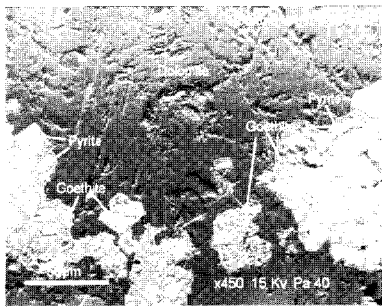
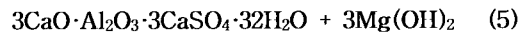
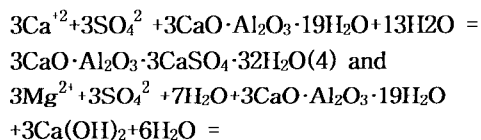


Fig. 5. SEM micrograph showing the oxidation of large pyrite inclusions in dolomite aggregate from Portland West quarry, I 35. Note the large pyrite mass on right side of photograph. Oxidation occurs on its outer surface and along fractures. The pyrite mass shown on the left side of photograph has been almost entirely replaced by goethite.

**Ettringite-forming reactions.**

Sulfate ions released by pyrite oxidation or other sources may exist with dissolved magnesium released during dedolomitization, reaction (1), or with dissolved calcium released by reaction (3). These ions can migrate outward into the cement paste and react with cement paste components such as C<sub>3</sub>A and calcium hydroxide (CH) to form ettringite by reaction (4), or ettringite and brucite by reaction (5):



Other minerals including gypsum could precipitate as intermediate phases, but no gypsum was observed in the EDAX element maps of any concrete sample. The lack of gypsum suggests that conditions in Iowa highway concrete are not favorable for its formation. Although both of the above reactions involve solid C<sub>3</sub>A and CH, two possible reaction mechanisms have been suggested for the reactions between ions in pore solutions and these cement paste components. The proposed reactions are: (1) topochemical (Chatterji and Jeffery, 1963; Cohen, 1983) and (2) through solution (Chatterji, 1976; Metha, 1976a; Deng and Tang, 1994; Fu and Beaudoin, 1996). Topochemical reactions have already been discussed. Monteiro (1985) defined the "through solution" mechanism as "the cement compounds dissolve to produce ions in solution that will recombine to form hydration products which subsequently precipitate out from supersaturated solution," (i.e. direct precipitation from solution).

Ettringite in Iowa highway concretes mainly grew in air entrainment voids, interstitial pore spaces, and pre-existing cracks that are not closely associated with aluminate particles. Occasionally it occurs in cracks between cement paste and coarse or fine aggregate. The characteristic occurrences of ettringite in open spaces without associated C<sub>3</sub>A or CH reacting particle locations indicate that a solution precipitation ("through solution") rather than a topochemical reaction was involved in its formation. The acicular habit of ettringite in entrainment voids is another indication of solution-precipitation reaction for its formation since it is generally accepted that crystals precipitating from supersaturated solutions are often elongate along their principal crystallographic axis (Metha, 1976b). In rare instances, ettringite

(5-10 $\mu$ m size) was observed under high-magnification, in association with aluminate particles that appear to be partly consumed by ettringite.

The larger accumulation of ettringite in older concretes compared to younger concretes may be related to the amount of deicer applied during winter months (Table 1). Older highways have received more deicer applications over their many years of use than younger highways. An example of this is the abundant ettringite in concrete of US 218 that was constructed using Paralta dolomite aggregate, which contained very low amounts of S (0.04 wt. %). The sulfur generated from the combustion of motor fuels may have also contributed to ettringite formation in older highway deterioration, but its significance is unclear. More abundant ettringite in older concrete than younger ones may also be a result of longer reaction times that produce more ettringite.

## EXPANSION MECHANISMS CAUSING IOWA HIGHWAY CONCRETE DETERIORATION

### Brucite-Induced Expansion in Iowa Concretes

Many studies concluded that brucite growth is at least partly responsible for expansion and concrete deterioration. Durand et al. (1992) experimentally observed that alkali-aggregate reactions generate expansion with stresses of 4.4 MPa. Tang et al. (1991) and Deng and Tang (1993) calculated the amount of expansion based on the solid volume changes associated with dedolomitization by using molar volume data of dolomite, calcite, brucite, and portlandite which are 64.34, 36.93, 24.63 and

33.06 cm<sup>3</sup>/mol, respectively. Their calculations showed that dedolomitization reactions (1) and (2) result in a net 7.5 % volume increase. However, Deng and Tang (1993) calculated that newly formed calcite/ brucite crystalline masses have a 25.95 % porosity under an assumption of tight-packing of equant spheres of brucite and calcite particles in restricted spaces. When porosity is included in calculations, a volume increase of 36.5 % results from the combined reactions (1) and (2). They concluded that this volume increase in the restricted spaces of reaction rims causes cracking because of internal stresses (Diab and Prin, 1992; Durand et al., 1992; Deng and Tang, 1993). SEM studies conducted herein reveal that significant amounts of brucite occur in the light-colored cement paste reaction zones and in dolomite aggregate reaction zones in concretes constructed with reactive dolomite coarse aggregate, but that more secondary calcite than brucite forms in these regions. In Iowa highway concrete samples, however, macro- or micro-cracking is not closely associated spatially with aggregate reaction rims (i. e., cracks only rarely occur at or parallel to aggregate-paste interfaces where dedolomitization occurred).

Abundant relatively coarse, euhedral to irregular shaped, brucite crystals occur in reactive aggregate concrete in the less altered cement matrix outside of Zone D (Fig.1). This study, however, found no evidence for significant volume increases associated with brucite. These crystals result from either topochemical replacement of portlandite crystals (reaction 3) or from direct precipitation of brucite in microscopic voids. The observations best support topochemical reactions with resultant volume decreases for microscopic brucite formation. If direct precipitation took place, a volume increase with expansion

cracking associated with the formation of brucite crystals should be expected (Tang et al., 1991; Deng and Tang, 1993). If topochemical replacement of portlandite with brucite occurred, there should be a 25 % volume decrease that should cause void space generation in areas of cement associated with brucite crystals and a lack of expansion cracking. As shown in the SEM micrograph (Fig.2), open spaces are associated with irregular shaped brucite masses in the cement matrix, and no observable cracking is spatially associated with the brucite.

Observations that cracking is not spatially related to brucite locations are not conclusive evidence against brucite-induced expansion because concretes containing abundant brucite also exhibit significant micro cracking and occasionally larger cracks. If brucite formation causes expansion and cracking in Iowa concretes, then it has been demonstrated that cracking must result from generalized stresses built up within macroscopic concrete masses. These stresses are relieved by cracking along weak directions and zones rather than in close proximity to newly formed brucite crystals.

#### **Ettringite-Induced Expansion in Iowa Concretes**

The formation of ettringite is believed by many researchers to cause expansion of concrete and deterioration by cracking of concrete. There is no doubt about the occurrence of delayed ettringite in severely deteriorated concrete but the mechanism of expansion remains controversial (Mather, 1984). Two principal hypotheses of ettringite-related expansion mechanisms have been proposed: (1) the crystal growth theory and (2) the swelling theory. In contrast to the above two hypotheses, which propose that ettringite is involved in expansion-related concrete damage,

another hypothesis proposes that ettringite growth is only indirectly responsible for expansion and cracking (Diamond, 1996). Ettringite growth typically involves loss of air-entrainment void space by crystal filling. According to Diamond (1996), the complete filling of air-entrainment voids by ettringite may cause loss of void effectiveness in preventing freeze damage to concrete during freezing/ thawing cycles. Freezing solutions are prevented access to air-entrainment voids because of filling or sealing by ettringite, and ice expansion will cause cracking.

It has been proposed that ettringite crystals formed in open space cannot cause expansion, and only the growth of ettringite in confined space can cause severe expansion. However, Shayan and Ivanusec (1996) suggested that void lining ettringite in open spaces may develop fine micro cracks during dry intervals and crystallization pressure can develop during precipitation of additional ettringite when liquid fills micro-cracks under moist conditions.

Abundant ettringite crystallized in the interstitial pore spaces, pre-existing cracks, and air-entrainment voids in Iowa highway concrete. This characteristic occurrence of ettringite, in pre-existing open spaces without association with reacting particle locations indicates that direct precipitation ("through solution") is the major reaction mechanism involved in its formation. Topochemical reactions may be partially responsible for extremely small ettringite crystals disseminated within the cement paste.

SEM analysis revealed that the cracks are spatially associated with void-fill and void-rim type ettringite. These expansion cracks originate from ettringite within entrainment voids and extend into the cement paste. The fact that ettringite does not fill these paste cracks and, in most case, no cracks propagate

through the ettringite filling voids, indicates that the cracks formed late in origin and developed after ettringite crystallized. Although ettringite can easily be observed in large open spaces in the cement paste using SEM/ petrographic microscope, ettringite probably also fills microscopic interstitial pore spaces in the cement paste before it fills large open spaces. Assuming that ettringite fills sub-microscopic interstitial pore spaces in the cement paste, the expansion mechanism of ettringite causing the deterioration of Iowa highway concretes can be suggested as follows: (i) expansion pressures develop because of volume increases during growth of ettringite that completely fills microscopic interstitial voids and small air-entrainment voids. These pressures result from either crystal growth or water absorption, (ii) void-fill and void-rim ettringite in larger interstitial pores and entrainment voids causes loss of void effectiveness in preventing freezing damage when the concrete is water saturated.

## 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 ( $\text{SO}_4^{2-}$ ) derived from pyrite oxidation significantly 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  $\text{C}_3\text{A}$  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.

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