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The formation and role of ettringite in Iowa highway concrete deterioration

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Abstract

Some Iowa highway concrete constructed of coarse carbonate aggregate exhibits premature deterioration, which is, in part, caused by the growth of secondary minerals, including ettringite. Petrographic scanning electron microscope (SEM) and energy-dispersive analytical X-ray (EDAX) studies were conducted to determine the abundance, spatial location, and morphology of ettringite and the spatial relationship of ettringite to the occurrence of oxidized pyrite and coarse/fine carbonate aggregate.

In poorly performing concrete ($<$ 16-year service life), ettringite completely fills many small voids, occurs as rims lining the margin of larger air entrainment voids and as microscopic disseminations in the paste. Pyrite (FeS_2) is commonly present in coarse aggregate, and goethite [FeO(OH)], one of its oxidation products, is observed in many concrete samples. Sulfate ions derived from pyrite oxidation apparently contribute to ettringite formation. The direct precipitation of ettringite from solution was responsible for most of the observed ettringite in voids and cracks. Microscopic ettringite, which commonly occurred in the paste, most likely was formed by the replacement of calcium aluminate. Severe cracking of cement paste is often spatially associated with ettringite, which strongly suggests that ettringite contributed to cracking and resultant deterioration.

Keywords: Ettringite; Chemical environment; Delayed ettringite formation (DEF); Long term performance

1. Introduction

A significant problem associated with highway deterioration is the relative importance of expansion resulting from secondary minerals formed in concrete. Certain concrete highways in Iowa containing carbonate coarse aggregate show premature deterioration that apparently is caused by secondary mineral growth. 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 formation in some Iowa highway concretes is produced by magnesium released via the dedolomitization of reactive dolomite coarse aggregates, as documented by Gan et al. [1] and Lee et al. [2].

The other potentially important deleterious mineral is ettringite that formed long after the concrete hardened. This variety of ettringite is referred to as delayed or secondary ettringite [3]. The formation of delayed ettringite is believed by many researchers to cause the expansion of concrete, but the mechanisms involved in the expansion remain controversial [3–11]. Delayed or secondary ettringite formation is especially enhanced by the availability of sulfate, which can be derived either from internal or external sources. One internal source is pyrite (FeS_2) that is present in coarse and fine aggregates in some Iowa highway concretes. Sulfate ions released by its oxidation may contribute to delayed ettringite formation (DEF) [12].

Two phases of study were undertaken to identify the mechanisms of DEF and its potential role in premature deterioration. In the first phase, petrographic and SEM/EDAX analyses were performed to determine the abun-

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dance, spatial location, and the characteristics of ettringite in addition to the spatial relationship of oxidizing pyrite in coarse/fine aggregate to ettringite occurrence. In the second phase, concrete deterioration was produced experimentally by immersing Iowa highway concrete samples in a sodium sulfate solution to further explore the role of ettringite in cracking. In addition, as part of the second phase, a study of the effects of chemical environment on ettringite crystallization was performed. Results of the first phase only will be discussed in this study, as those from the second phase are reported elsewhere [13].

2. Methods of study

Cores were collected from 10 different Iowa concrete highways with different service records and containing limestone/dolomite coarse aggregate from different quarries (Table 1). Nine of the cores were from poorly performing highways (i.e., service life of <16 years). One durable concrete containing Sundheim coarse aggregate (Sample F) was also included. Each of the 4-in.-diameter concrete highway cores was cut into small rectangular blocks, 2 × 2 × 4 cm. Polished thin sections were made from blocks from the top (1 in. below the road surface) and bottom (1 in. from the bottom of the concrete layer) and studied with a standard petrographic microscope using transmitted and reflected light. Petrographic examination was used to identify specific areas to be studied with a scanning electron microscope (SEM) and to supplement the observations of features, such as paste and aggregate color variations, that cannot be observed with a SEM.

A Hitachi S 2460 reduced-vacuum SEM was used, and back-scattered images were obtained. Energy-dispersive analytical X-ray (EDAX) area maps were obtained for Si, Al, K, Na, O, Ca, Mg, S, Cl, and Fe. EDAX point analyses were obtained at high magnification to identify mineral compositions. An accelerating voltage of 15 kV was used for imaging and 20 kV for EDAX point analyses.

3. General features of Iowa highway concrete samples

3.1. Dolomite coarse aggregate

3.1.1. Crystallinity and crystal size

Two types of dolomite were distinguished by petrographic and SEM observations. They are referred to as ‘‘reactive’’ and ‘‘nonreactive’’ dolomite coarse aggregates. When reactive dolomite coarse aggregate is used in highway construction, reactions between the aggregate particles and cement paste produce reaction rims related to the process of dedolomitization [1,14]. These partially dedolomitized rims are clear evidence of reactive dolomite. A calcified paste region typically surrounds partly dedolomitized aggregate particles. The calcite produced was apparently derived from dedolomitization because it does not commonly surround the nonreactive coarse aggregate. SEM, EDAX, and petrographic microscope studies showed that durable concrete made with nonreactive dolomite coarse aggregate exhibited little evidence of rim development, no visible cracking, and little secondary ettringite in field samples, whereas nondurable concrete containing reactive coarse aggregate commonly exhibited rims, extensive cracking, and abundant ettringite in voids [15].

Bulk chemical analyses of dolomite coarse aggregate used in the concrete were provided by the Iowa Department of Transportation (IDOT) and show that dolomite aggregates in durable and nondurable concretes have no major differences in chemical composition. Analyses indicate that all the dolomite aggregates contain approximately 20 wt.% MgO and 30 wt.% CaO, which is close to the theoretical composition of dolomite, 21.86 and 30.41 wt.%.

It was possible to distinguish the two dolomite types on the basis of crystal size and morphology (i.e., crystallinity; [1,14,16–19]). Reactive dolomite aggregate consists of mostly fine-grained, anhedral dolomite crystals with many small void spaces between loosely intergrown crystals, whereas nonreactive dolomite aggregate typically consists of coarse-grained, euhedral dolomite crystals that are tightly intergrown and that are essentially free of voids.

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

Sample number	Core location	Year[a]	Coarse aggregate source	Portland cement
A	I 35, Cerro Gordo	1974	Portland West quarry, Shellock Fm.	Northwestern I
B	US 30, Linn	1981	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Lehigh I
C	IA 9, Howard	1974	Dotzler quarry, Spillville Fm.	Lehigh I
D	IA 21, Iowa	1982	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Martin Marietta (?)
E	US 63, Howard	1971	Nelson quarry, Cedar Valley Fm.	Dewey I
F	US 20, Dubuque	1988	Sundheim quarry, Hopkinton Fm.	Davenport I
G	IA 100, Linn	1989	Crawford Lee quarry, Spring Grove Member, Wapsipinicon Fm.	Continental III
Gan-1	US 63, Tama	1972	Smith quarry, Coralville Member, Cedar Valley Fm.	Lehigh I
Gan-2	US 151, Linn	1947	Paralta quarry, Otis Member, Wapsipinicon Fm.	Mixed (Medusa, Lehigh, Dewey, Atlas, Alpha)
Gan-3	US 218, Benton	1971	Garrison quarry, Coralville Member, Cedar Valley Fm.	Davenport I
Gan-4	US 20, Dubuque	1988	Sundheim quarry, Hopkinton Fm.	Davenport I

[a] Year the highway was constructed.

3.1.2. Pyrite inclusions

When rocks containing sulfur-bearing minerals are used for aggregate in concrete, they serve as potential sources of sulfate for the formation of secondary ettringite [12,20–22]. Of these sulfur-bearing minerals, pyrite (FeS_2) is the more common in dolomite and limestone aggregates used in Iowa highway concretes. Large quantities of magnesium sulfate efflorescence have been noted on the surfaces of pyritic dolomites present in several Iowa concrete cores [23], thus demonstrating that pyrite has oxidized in concrete paste to produce sulfate and that the concretes contain a large amount of soluble magnesium derived from dolomite.

The sulfur content of dolomite aggregate varies from 0.03 to 0.62 wt.%. Small pyrite inclusions (< 10 μm) are primarily disseminated within dolomite and limestone aggregates, whereas coarser pyrite crystals (>50 μm) are present in some aggregates (Fig. 1). The pyrite is often either partially or completely oxidized to goethite [FeO(OH); Fig. 1].

3.2. Fine aggregate

In the Iowa highway concretes studied, about 25 to 35 vol.% of the concrete consists of fine aggregate (<2.5 mm in diameter), which is chiefly quartz, with minor amounts of orthoclase, clay minerals, biotite, amphibole, goethite, and limonite. A small number of fine aggregate particles containing a matrix of pyrite that is partially oxidized to goethite were observed in many samples.

3.3. Cement paste

3.3.1. Chemical composition

Six different varieties of Portland cement were used in the construction of the Iowa highway concretes that were studied (Table 1). All of the cements were Type I (normal Portland cement), except for one that was Type III, high early strength cement. This was continental III cement, used in the construction of IA 100 (Sample G). Bulk chemical analyses of the cements were obtained by the Iowa DOT, and the average, standard deviation, and maximum and minimum values of duplicate analyses are listed in Table 2. In this table, the last column, “Potential Compound Composition,” refers to the maximum compound composition allowable by ASTM C150 Bogue [24] calculations. The Type I cements contain 2.71 to 3.16 wt.%, and the Type III cement had a somewhat higher content of 3.57 wt.% SO_3.

3.3.2. Air-entrainment voids

All of the Iowa highway concretes studied contained similar volume quantities of entrained air voids ($6\% + 1^{1/2}$ vol.%) that are, more or less, uniformly distributed through

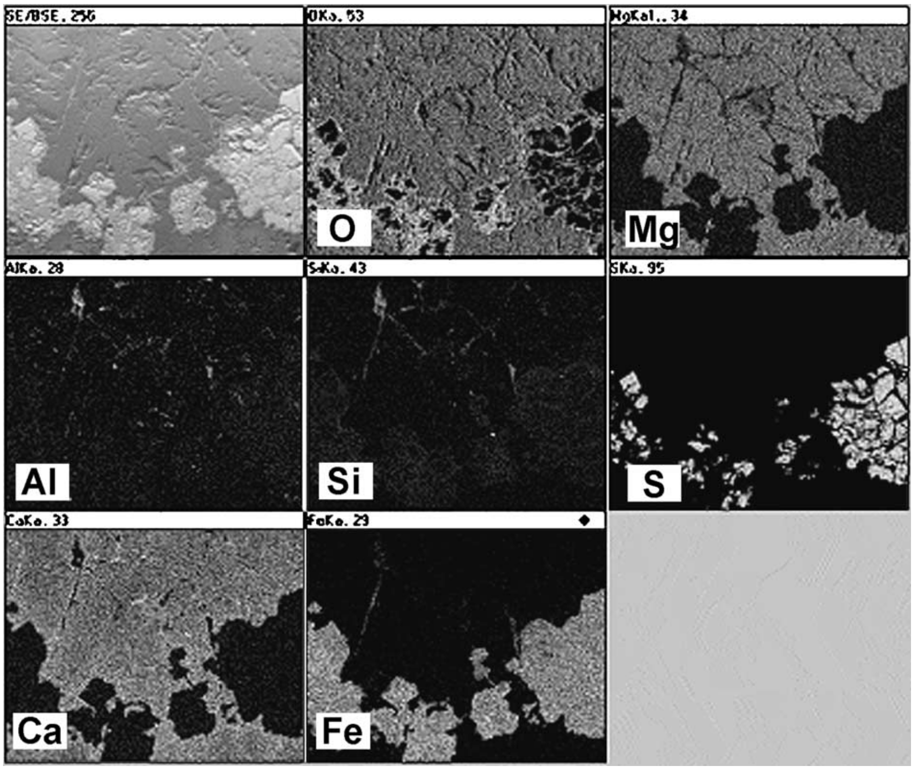

Fig. 1. EDAX maps showing the oxidation of large pyrite inclusions in dolomite aggregate from Portland West quarry, I 35 (Sample A). Note the large iron- and sulfur-rich pyrite mass on the right side of the micrograph. Oxidation occurs on its outer surface and along fractures. The pyrite mass shown on the left side of micrograph has been almost entirely replaced by goethite, as seen by comparing the iron, oxygen, and sulfur EDAX images.

Table 2
Composition of portland cement used for Iowa highway concretes

Name of portland cement		Chemical composition (%)						Na_2O equiv.	Loss of ignition (%)	Insoluble residue (%)	Total	Potential compound composition (%)			
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3					C_3S	C_2S	C_3A	C_4AF
Davenport (Type I)	Average	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
	S.D.	1.23	0.39	0.39	1.17	0.50	0.24	0.12	0.31	0.20					
	Maximum	24.76	6.65	4.14	65.45	4.65	3.4	0.94	2.07	1.28					
	Minimum	17.09	2.92	2.16	55.1	1.57	1.97	0.37	0.44	0.02					
Continental (Type I)	Average	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	6.83
	S.D.	1.15	0.62	0.53	1.10	0.67	0.34	0.21	3.53	0.16					
	Maximum	24.24	6.14	3.39	67.61	5.12	4.23	0.83	3.01	0.92					
	Minimum	19.07	2.58	1.3	61.34	2.01	2.44	0.01	0.44	0.00					
Continental III (Type III)	Average	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
	S.D.	0.33	0.14	0.01	0.36	0.17	0.17	0.02	0.11	0.10					
	Maximum	20.94	5.14	1.39	64.30	3.52	3.71	0.12	1.38	0.35					
	Minimum	20.27	4.82	1.36	63.47	3.14	3.33	0.07	1.13	0.12					
Lehigh (Type I)	Average	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
	S.D.	1.36	0.36	0.21	1.39	0.55	0.23	0.12	0.35	0.36					
	Maximum	25.57	6.09	3.37	67.18	4.72	3.78	0.82	1.81	2.66					
	Minimum	18.05	3.36	2.03	60.37	0.95	2.22	0.40	0.17	0.03					
Northwestern (Type I)	Average	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
	S.D.	1.59	0.31	0.46	1.15	0.71	0.28	0.14	0.33	0.13					
	Maximum	24.53	5.51	3.1	67.44	4.22	3.67	0.81	2.15	0.69					
	Minimum	18.68	3.78	1.55	62.05	1.15	2.05	0.21	0.4	0.03					
Martin Marietta[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	N/A
Dewey I[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	N/A

[a] Chemical composition data were not available from DOT.

the cores. Microscopic thin-section observations show that air entrainment voids are spherical, with diameters varying from several tens of microns to several millimeters. Ettringite commonly occurs in the entrainment voids of the nondurable concretes.

4. Results

4.1. Ettringite in Iowa highway concretes

4.1.1. Occurrence

In Iowa highway concrete samples studied, two forms of ettringite occurred in air-entrainment void spaces as needle-like crystals projecting from the void walls (Fig. 2). The first form of ettringite is referred to as “void-fill” ettringite, which completely fills smaller air-entrainment voids <100 μm in diameter (Fig. 3). Abundant irregular cracks occur in the ettringite filled voids. The second form of ettringite is referred to as “void-rim” ettringite, which occurs around the interior margins of voids and consists of coarser crystals. This type of ettringite usually occurs in air-entrainment voids >100 μm in diameter. Radially oriented microcracks are prominent in the ettringite rims. Some of the cracks in both void-fill and void-rim ettringite continue into the cement paste. The formation of the two types of ettringite depends upon the size of the void space and the amount of ettringite-forming pore solutions that passed through the voids. Thus, the degree of filling depends chiefly on void size and time. Partly filled voids developed as ettringite-precipitating pore solutions continued to percolate through the voids. In some regions, ettringite also fills microscopic interstitial pores in the cement paste (Fig. 4). Because of its small size, interstitial ettringite is only observed in high-magnification back-scattered SEM images. Rarely, ettringite also occurs in cracks that formed along the boundary between the paste and fine quartz aggregate particles (Fig. 5). High-magnification SEM shows that ettringite does not occur in microcracks that extend from ettringite-filled voids into the concrete paste (Figs. 3 and 4). The lack of ettringite in these microcracks provides strong evidence that the microcracking associated with void fill/rim ettringite developed after the rims or voids were lined with ettringite.

4.1.2. Ettringite and pyrite inclusions

4.1.2.1. Pyrite oxidation reactions. Evidence of pyrite oxidation in cement samples is suggested by the presence of iron oxides, predominantly goethite, followed by ferrihydrite [$Fe(OH)_3$], in the form of partial or complete pseudomorphs of preexisting pyrite (Fig. 1). The oxidation of pyrite is a complex process involving a number of reactants and products under varying pH and oxygen fugacity. Part of the observed pyrite oxidation in our samples may have occurred long before the coarse aggregate was quarried, but some oxidation also developed after pyrite-containing aggregate was incorporated into the highway concrete.

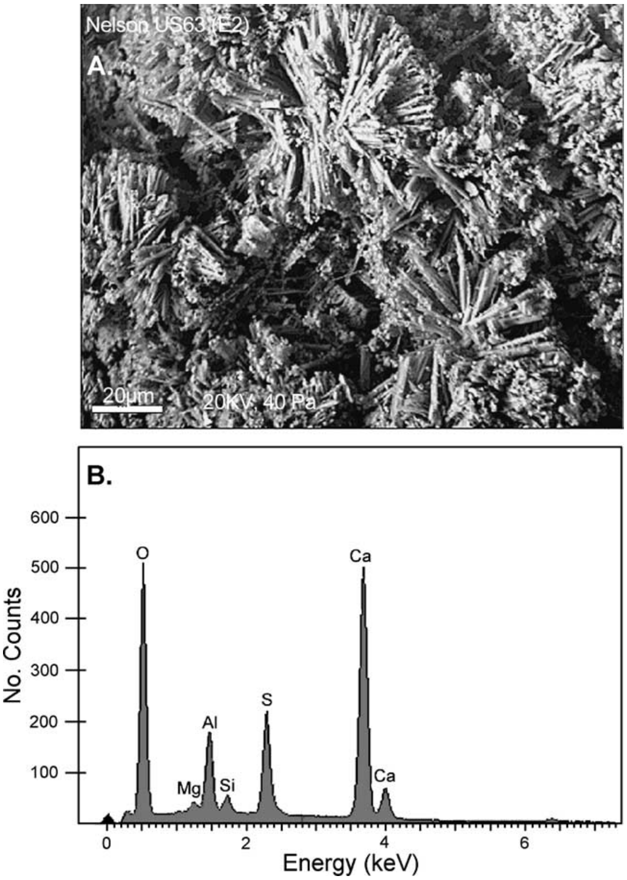

Fig. 2. (A) SEM view of acicular ettringite crystals in paste from Iowa highway concrete, US 63 (Sample E). (B) Energy-dispersive X-ray analysis of the crystals reveals strong Ca, Al, and S peaks that confirm that these crystals are ettringite. The occurrence of a weak Si peak indicates that Si partially substitutes for Al in the ettringite structure.

The major reactions involved in pyrite oxidation under alkaline concrete-forming conditions are:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O = \underset{\text{Ferrihydrite}}{Fe(OH)_3} + 2\ SO_4^{2-} + 4\ H^+ \quad (1)$$

$$FeS_2 + 15/4\ O_2 + 5/2\ H_2O = \underset{\text{Goethite}}{FeO(OH)} + 2\ SO_4^{2-} + 4\ H^+ \quad (2)$$

$$FeS_2 + 15/4\ O_2 + 2\ H_2O = \underset{\text{Hematite}}{1/2Fe_2O_3} + 2\ SO_4^{2-} + 4\ H^+ \quad (3)$$

Volume changes associated with 1, 2, and 3 are +3.05, −3.12, and −8.81 cm^3/mol sulfide, respectively, and have been to referred as “primary expansion” due to pyrite oxidation [22]. A stability diagram for pyrite (FeS_2), siderite [$Fe(CO_3)$], ferrihydrite [$Fe(OH)_3$], calcite [$CaCO_3$], and gibbsite [$Al(OH)_3$] and aqueous species is presented in Fig. 6. As shown in the diagram, ferrihydrite is the predominant pyrite oxidation product under the alkaline conditions that prevail in moist concrete. Ferrihydrite may subsequently transform into goethite by dehydration:

$$Fe(OH)_3 = FeO(OH) + H_2O \quad (4)$$

Further dehydration could produce hematite via:

$$2FeO(OH) = Fe_2O_3 + H_2O \quad (5)$$

Reaction 5 seems unlikely to occur in highway concrete because this reaction requires low moisture, and water is generally retained in concrete [22]. Reactions 2 and 3 are probably predominant in highway concretes. As a result of pyrite oxidation, acid generation may cause transient, relatively low, strongly localized microenvironmental pH

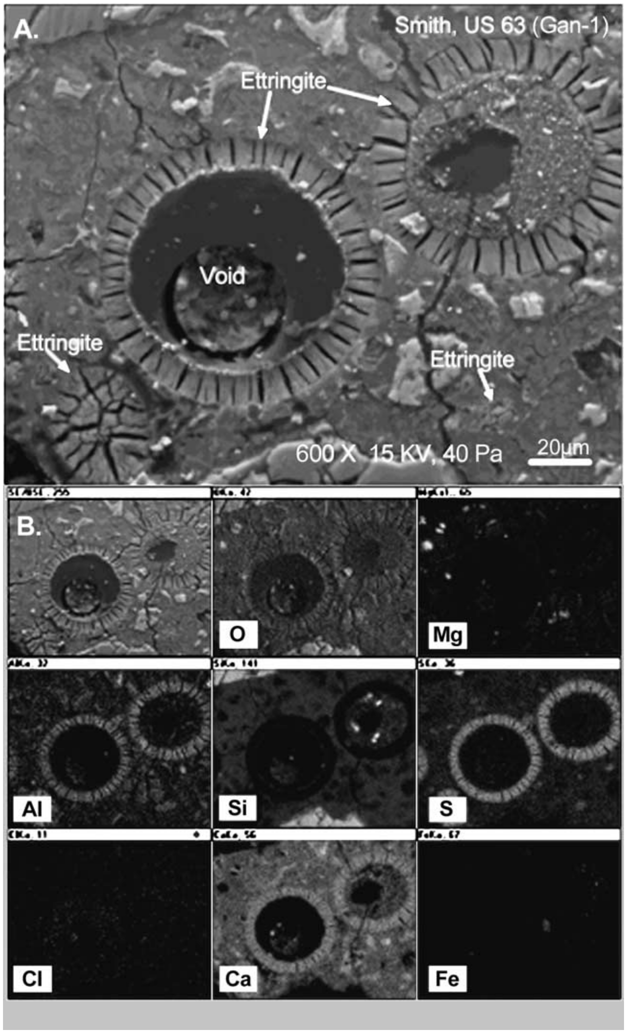

Fig. 3. (A) SEM micrograph and (B) EDAX maps showing both air-entrainment voids with void-rim and void-fill types of ettringite (Sample E). Void-rim ettringite occurs as a rim that lines the margin of air entrainment voids (>100 µm) in the cement paste. Radial cracks are well developed in this type of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

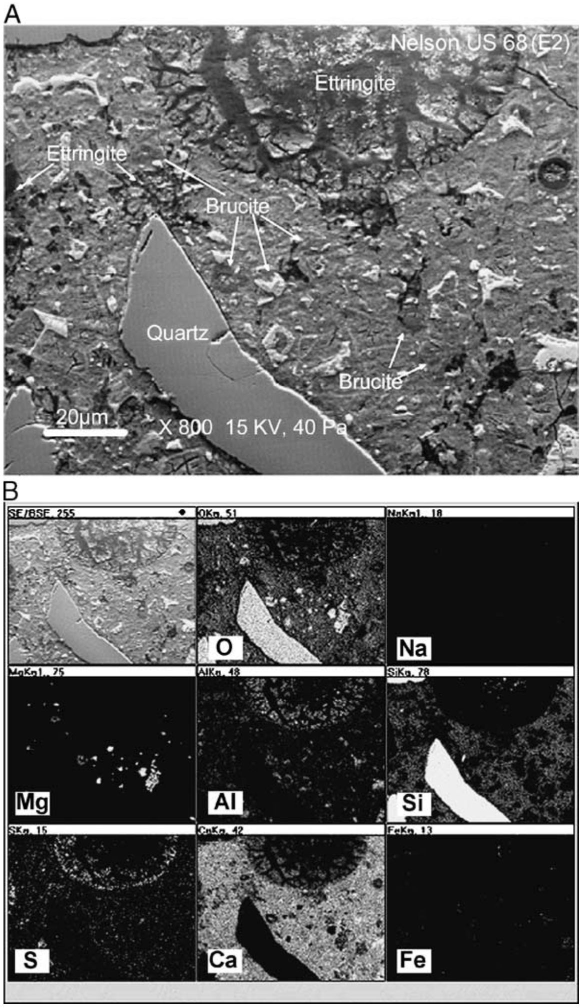

Fig. 4. (A) SEM micrograph and (B) EDAX area maps showing the brucite and ettringite formation in the unaltered cement paste (Sample E). Small brucite crystals, <20 μm size, occur in irregular-shaped nodules in the cement matrix. Note that open spaces are developed in the vicinity of brucite. Ettringite completely fills the large air-entrainment voids and interstitial pores in the cement paste. Cracks developed in the 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.

conditions surrounding the oxidation products. Typically, in concrete, and always in dolomite or limestone aggregates, pore solutions are saturated with carbonate so that a buffer system is maintained. Under these conditions, hydrogen ions generated by pyrite oxidation are neutralized by combining with CO_3^{2-} to form bicarbonate (HCO_3^-), with the pH remaining essentially constant, except for very short time intervals or under unusual local conditions [25]. Transient depressed pH conditions, even of brief duration, however, could significantly influence dedolomitization reactions.

4.1.3. Ettringite spatial relationships

More ettringite occurs in the cement paste near dolomite aggregates that contain many oxidized pyrite inclusions than occurs near aggregate without pyrite. In turn, the degree of pyrite oxidation depends upon the coarse carbonate aggregate properties and pyrite location in the coarse aggregate. The accessibility of oxidizing pore solution to pyrite in coarse dolomite aggregate is affected by the dolomite crystal size, degree of crystallinity, porosity, and reactivity of the coarse aggregate. Pyrite inclusions adjacent to open spaces, such as interstitial pores or intercrystalline boundaries, typically are well oxidized because oxidizing solutions have easier access to pyrite through the open spaces and along grain boundaries. Pyrite that is completely enclosed within large, well-crystallized dolomite crystals is not typically oxidized because pyrite has little chance of exposure to oxidizing solutions. The volume and amount of void space in dolomite coarse aggregate also varies with aggregate type. Open spaces are common in fine-grained,

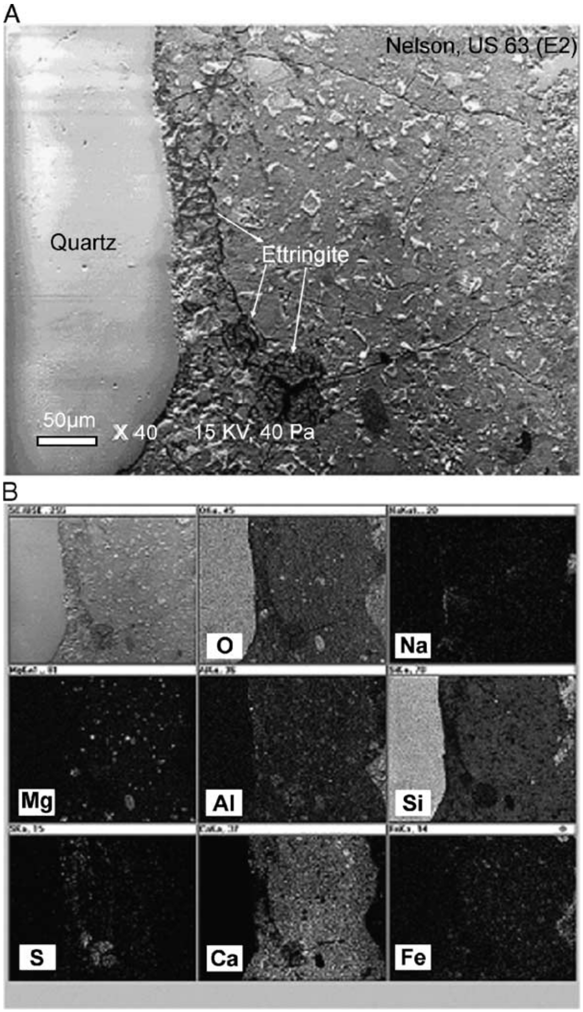

Fig. 5. (A) SEM micrograph and (B) EDAX maps showing ettringite in preexisting cracks (Sample E). Ettringite forms along the preexisting cracks between quartz aggregate and cement paste. The cracks appear to be formed by expansive alkali–aggregate reaction. Microcracks extend from ettringite into the cement paste.

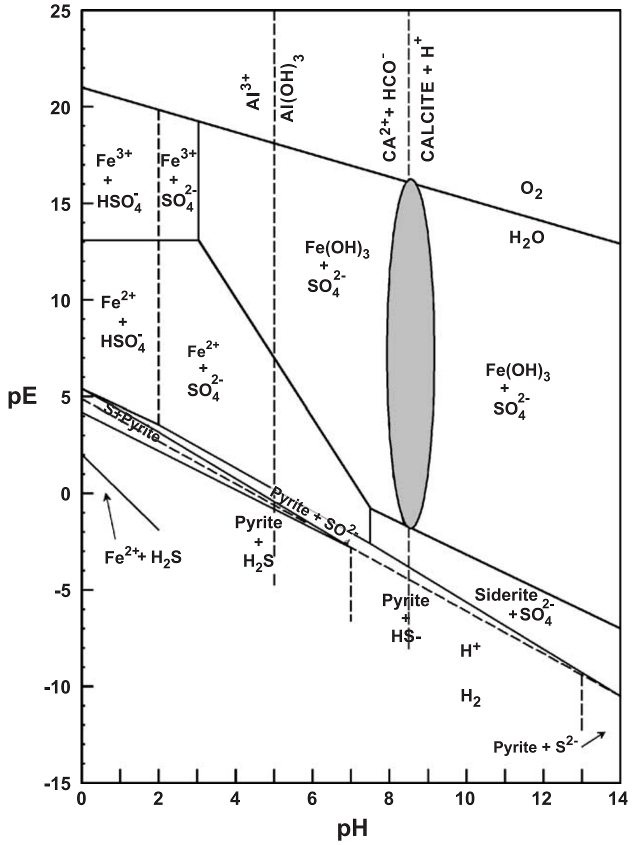

Fig. 6. A stability diagram for selected iron minerals at 25 °C and $\Sigma Fe = 10^{-4}$, $\Sigma S = 10^{-2}$, $\Sigma Ca = 10^{-4}$ mol/l, and $PCO_2 = 10^{3.5}$ bar. The shaded area indicates the probable pE–pH values associated with calcite dissolution in pore water (after Chinchon et al. [21]).

poorly crystallized dolomite aggregate, whereas they rarely occur in coarse-grained, euhedral crystal aggregates. Fine-grained dolomite is also more amenable to dedolomitization than is the coarse-grained dolomite, and this reaction produces secondary void spaces that promote pyrite oxidation. Pyrite in the dedolomitization reaction rims of reactive dolomite coarse aggregate is usually well exposed to oxidizing solutions and, consequently, is usually more oxidized compared with pyrite in nonreactive dolomite coarse aggregate margins.

5. Discussion

5.1. Evaluation of sulfur sources in Iowa concrete

5.1.1. External and internal sources

Sulfur sources for ettringite in highway concrete can be both external and internal. External sources include natural or polluted ground water, moisture in soils [26,27], and sulfate-rich acid rain. Other potential external sulfate sources are sulfur dioxide from the combustion of motor fuels and the sulfate impurities of deicing salt [28]. Internal sources of sulfate are the sulfate- or sulfide-bearing components of cement, coarse and fine aggregate, pozzolans, and admixtures that are in concrete. Cement blends and pyrite in coarse aggregate were the two internal sources of sulfur for ettringite formation that were evaluated semiquantitatively to determine whether those sources might be sufficient to cause the observed ettringite abundance in cement pastes. External sources of sulfur were not evaluated, although only relatively small amounts of ettringite occur near pyrite inclusions, thus suggesting that external sources of sulfur may also be required to account for all ettringite present. Road salt impurities may be a significant external source of sulfur. According to Pitt et al. [28], rock salt (NaCl) applied as a deicer on Iowa highways contains up to 4 wt.% sulfate impurities, present as gypsum and magnesium sulfate. These minerals dissolve, and their ions migrate downward into the concrete. The external sources of sulfur, such as deicer impurities, may be significant contributors to the formation of ettringite in Iowa highway concretes, although we did not observe a correlation of ettringite abundance with proximity to the top of road surfaces, as one might predict if applied deicers were major sources of sulfur. It may be, of course, that external-source sulfate ions migrate downward for considerable distances along fractures and slab boundaries before the sulfate reacts with the paste components to form ettringite. Similar considerations may apply to pyritic sulfate ion migration before ettringite precipitates.

5.1.2. Sulfur from cement blend

Portland cement blends in highway concretes contain relatively uniform SO_3 contents (2.71 to 3.57 wt.%; Table 1), which are well within the range of 2.5 to 4.0 wt.% SO_3 considered necessary to avoid secondary ettringite formation in concrete [24]. Consequently, there must be additional sources of sulfur to account for the secondary ettringite observed in our samples. The most significant internal source, in addition to that from cement blend, is pyrite that occurs in the concrete coarse aggregate. Our research documents that the amount of pyrite in the samples studied may be sufficient to account for the observed ettringite concentration (Table 3a and b).

5.1.3. Sulfur from pyrite

The maximum amount of sulfate that is derived from the oxidation of pyrite in dolomite coarse aggregate can be roughly estimated from the sulfur content of the aggregate and the mixing specifications for concrete using the following assumptions: (1) all sulfur in the coarse aggregate exists as pyrite, (2) all pyrite inclusions are oxidized and all oxidation occurred in the concrete environment, (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) is applicable to all the concretes, and (4) all SO_4^{2-} derived from pyrite migrates from the aggregate into the cement paste.

Table 3
Sulfur content (wt.%) in cement paste dolomite aggregate and maximum calculated SO_3 content (wt.%) of cement paste

Sample name	Aggregate source	Type of cement		SO_3 content in cement (wt.%)	S content in dolomite aggregate (wt.%)	Potential pyritic SO_3 (wt.%) in cement[a]	Potential total SO_3 (wt.%) in cement[b]
A (IA 35)	Portland West	Northwestern I	Mean	2.97	0.300	2.61	5.58
			S.D.	0.28	0.129	1.12	1.40
			Maximum	3.67	0.537	4.50	8.17
			Minimum	2.05	0.072	0.60	2.65
B (US 30)	Crawford Lee	Lehigh I	Mean	3.16	0.335	3.21	6.37
			S.D.	0.23	0.116	1.11	1.34
			Maximum	3.78	0.516	4.95	8.73
			Minimum	2.22	0.242	2.32	4.54
C (IA 9)	Dotzler	Lehigh I	Mean	3.16	0.304	2.92	6.08
			S.D.	0.23	0.050	0.8	1.03
			Maximum	3.78	0.398	3.82	7.60
			Minimum	2.22	0.225	2.16	4.38
D (IA 21)	Crawford	Martin Marietta	Mean	NA	0.335	3.21	NA
			S.D.	NA	0.116	1.11	NA
			Maximum	NA	0.516	4.95	NA
			Minimum	NA	0.242	2.32	NA
E (US 63)	Nelson	Dewey I	Mean	NA	0.257	2.60	NA
			S.D.	NA	0.189	1.81	NA
			Maximum	NA	0.684	6.56	NA
			Minimum	NA	0.060	0.58	NA
F (US 20)	Sundheim	Davenport I	Mean	2.71	0.026	0.21	2.92
			S.D.	0.24	0.003	0.03	0.27
			Maximum	3.40	0.022	0.25	3.65
			Minimum	1.97	0.003	0.04	2.01
G (IA 100)	Crawford	Continental	Mean	3.57	0.335	3.21	6.78
			S.D.	0.17	0.116	1.11	1.28
			Maximum	3.71	0.516	4.95	8.66
			Minimum	3.33	0.242	2.32	5.65
Gan-1 (US 63)	Smith	Lehigh I	Mean	3.16	0.337	3.23	6.39
			S.D.	0.23	0.131	1.26	1.49
			Maximum	3.78	0.493	0.47	4.25
			Minimum	2.22	0.174	1.67	3.89
Gan-2 (US 151)	Paralta	Mixed	Mean	NA	0.037	0.35	Na
			S.D.	NA	0.004	0.04	Na
			Maximum	NA	0.041	0.39	Na
			Minimum	NA	0.028	0.27	Na
Gan-3 (US 218)	Garrison	Davenport I	Mean	2.71	0.540	5.18	7.89
			S.D.	0.24	0.136	1.30	2.54
			Maximum	3.40	0.884	8.48	11.88
			Minimum	1.97	0.398	3.82	5.79
Gan-4 (US 20)	Sundheim	Davenport I	Mean	2.71	0.026	0.21	2.92
			S.D.	0.24	0.003	0.03	0.27
			Maximum	3.40	0.022	0.25	3.65
			Minimum	1.97	0.003	0.04	2.01

[a] This value represents the total wt.% of pyritic sulfur that could accumulate in the cement paste phase, given the assumptions given in text.

[b] This value is the sum of the SO_3 content in cement (wt.%) (Column 5) plus the potential pyritic SO_3 (wt.%) in cement (Column 7).

The estimated SO_3 content (wt.% of cement) that can be derived from the oxidation of pyrite inclusions in coarse dolomite aggregate is listed for each sample in Column 6 in Table 3, whereas the potential total SO_3 available for ettringite formation from the cement and the aggregate is listed in the last column. As given in Table 3, for example, calculations show that 0.3 wt.% (Column 6) of pyritic sulfur in the coarse dolomite aggregate can result in the addition of up to 2.61 wt.% of SO_3 (Column 7) in the cement paste of Iowa highway IA 35. The addition of SO_3 from pyrite oxidation will supplement that from the cement blend and will result in a higher sulfur content than recommended to prevent delayed or secondary ettringite formation. Consequently, the oxidation of pyrite-bearing coarse aggregate may promote ettringite-induced deterioration. Of course, the amount of ettringite formed will be less than the calculated maximum because all concrete samples contain both unoxidized and oxidized pyrite, and some oxidation may have occurred before the incorporation of the coarse aggregate into the concretes.

5.2. Ettringite-forming reactions

Sulfate ions released by pyrite oxidation or other sources may exist with dissolved magnesium released during dedolomitization reaction,

$$CaMg(CO_3)_2 + 2\ MOH = CaCO_3 + Mg(OH)_2 + M_2CO_3 \tag{6}$$

where M represents alkalis such as Na or K, or with dissolved calcium released by the reaction,

$$Mg^{2+} + Ca(OH)_{2(aq)} = Mg(OH)_2 + Ca^{2+} \tag{7}$$

These ions can migrate into the cement paste and react with the cement paste components, such as tricalcium aluminate (C_3A) and calcium hydroxide (CH), to form ettringite by Reaction 8, or ettringite and brucite by Reaction 9:

$$\begin{aligned} &3Ca^{2+} + 3SO_4^{2-} + 3CaO \cdot Al_2O_3 \cdot 19H_2O + 13H_2O \\ &\quad = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \end{aligned} \tag{8}$$

and

$$\begin{aligned} &3Mg^{2+} + 3SO_4^{2-} + 7H_2O + 3CaO \cdot Al_2O_3 \cdot 19H_2O \\ &\quad + 3Ca(OH)_2 + 6H_2O \\ &\quad = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3Mg(OH)_2 \end{aligned} \tag{9}$$

Other minerals, including gypsum ($CaSO_4 \cdot 2H_2O$), could precipitate as intermediate phases, but no gypsum was observed in the EDAX element maps of any of our concrete samples.

Two possible mechanisms have been suggested for the reactions between ions in pore solutions and cement paste components to form ettringite. They are *topochemical* [29,30] (=replacement of preexisting mineral phases) and *through solution* [10,31–36] (=direct precipitation from solution). Hansen [37] concluded that ettringite must have formed by a topochemical reaction because tricalcium aluminate does not dissolve in an aqueous medium and, consequently, could not be an aluminum ion source. He proposed that ettringite forms radially around residual topochemically reacting C_3A particles [30,38]. If the ettringite-forming reaction is topochemical, then there should be a definite relationship between the crystal structures of the reacting particles and that of ettringite [32,33,38]. Because of large difference in the crystal structures of ettringite (hexagonal) and anhydrous calcium aluminate (C_3A; cubic) or tetracalcium monosulfoaluminate (C_4A_3S; hexagonal), however, the topochemical reaction is considered by many workers to be kinetically difficult at normal temperatures [10,39]. Mehta [32] believed that the formation of ettringite on the surfaces of reacting particles and its random deposition in other locations is an indication of a through solution mechanism for precipitation rather than a topochemical one. Deng and Tang [10] assumed that the bonds of Ca–O and Al–O of aluminate are broken when polar H_2O molecules and/or OH^- ions interact with aluminate particles, and eventually, Ca^{2+} and $Al(OH)_4{}^-$ ions form in pore solutions. As a result of reactions between these ions and $SO_4{}^{2-}$ ions in solution, secondary ettringite preferentially precipitates in open spaces, such as voids and cracks as needle-like (acicular) crystals, whenever pore solutions are critically supersaturated [32,34,40,41]. Fu and Beaudoin [42,34] concluded that ettringite crystallization rates are controlled by the degree of supersaturation required to form critical-size nuclei of ettringite.

Ettringite in Iowa highway concretes mainly grew in air entrainment voids, interstitial pore spaces, and preexisting cracks and is not closely associated with aluminate particles. Occasionally, it occurs in cracks between cement paste and coarse or fine aggregate. The characteristic occurrences and morphology of ettringite in open spaces prove that direct precipitation from solution rather than a topochemical reaction was involved almost exclusively in the formation of the large ettringite crystals observed in this study. Also, the acicular habit (Figs. 2 and 3) of ettringite in entrainment voids contradicts a topochemical mechanism for its formation because it is generally accepted that crystals precipitating from supersaturated solutions are often elongate along their principal crystallographic axis [33]. Microscopic ettringite (5–10 μm in length) was observed in high-magnification SEM images in association with aluminate particles that appear to be partly consumed by ettringite and may be topochemical in origin. However, this type of ettringite is comparatively uncommon compared with void-fill/rim ettringite.

Freeze/thaw conditions may also enhance ettringite formation. Day [40] proposed that the freezing of capillary pore solutions in highway concrete plays a significant role in ettringite formation in larger voids. He concluded that pore solutions could be expelled by osmotic pressure during freezing of the concrete pore solutions from capillaries into larger voids where conditions are favorable to coarser ettringite crystals. Day [40] also pointed out that a reduction in $Ca(OH)_2$ concentrations in solution results in an increase in ettringite solubility. In the Iowa highway concrete studied, the formation of calcite in reaction zones of the cement paste locally depletes $Ca(OH)_2$ and thereby may facilitate ettringite dissolution. This observation may partly explain the near absence of ettringite in cement-phase dedolomitization reaction rims.

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

5.3. Ettringite-induced concrete expansion

5.3.1. Expansion mechanisms

Ettringite is believed by many researchers to cause the expansion and cracking of concrete, and numerous studies have been conducted to identify the mechanism of ettringite formation and expansion [3–11,30,34,43–55]. There is no doubt about the presence of delayed ettringite in severely deteriorated concrete, but some researchers have proposed that it simply forms more abundantly in cracked concrete because of more rapid movement of ettringite-bearing solutions [47].

Two principal hypotheses of ettringite-related expansion mechanisms have been proposed: (1) the crystal growth theory and (2) the swelling theory. These theories are discussed in detail by Cohen [9] and Diamond [11]. Cohen [30] suggested a model of expansion by crystal growth in which expansion is caused by crystal growth pressures exerted by ettringite crystals growing on the surface of Al-bearing particles. With this model, large crystals will be more expansive than small ones. Diamond [11] supported this hypothesis and presented a thermodynamic argument for ettringite crystal growth pressures.

Mehta [5], on the basis of his experiments, suggested an alternative hypothesis for expansion. According to Mehta and Hu [6] and Mehta and Wang [45], expansion is caused by water adsorption on the negatively charged surfaces of ettringite. With this model, the greatest expansion of ettringite is to be expected from smaller crystals, especially from colloidal ettringite, which may create significant expansion because its immense surface area can adsorb large quantities of water on a per weight basis.

In contrast to the above two hypotheses, which proposed that ettringite is involved in expansion-related concrete damage, another hypothesis proposed by Diamond [11] is that ettringite growth is only indirectly responsible for expansion and cracking. Ettringite growth, typically in air-entrainment voids, produces loss of void space. According to Diamond [11], the complete filling of air-entrainment voids by ettringite may cause a loss of void effectiveness in preventing freeze damage to concrete during freeze/thaw cycles. Freezing solutions are prevented access to air-entrainment voids because of filling or sealing by ettringite, and ice expansion will cause cracking.

5.3.2. Ettringite and expansion in Iowa concretes

In the Iowa highway concrete studied, abundant ettringite crystallized in the interstitial pore spaces, older cracks, and air-entrainment voids. This characteristic occurrence of ettringite in preexisting open spaces without association with reacting particle locations indicates that direct precipitation is the major reaction mechanism involved in its formation. Topochemical reactions may be partially responsible for very small ettringite crystals (microscopic and submicroscopic) disseminated within the cement paste. Although microscopic ettringite can be seen with a high-magnification SEM, it does not seem abundant enough to play a major role in expansion mechanisms.

The expansion mechanisms involving ettringite that produces the deterioration of Iowa highway concretes can be suggested as follows: (1) expansion pressures develop because of volume increases during growth of ettringite that completely fills microscopic interstitial voids and small air-entrainment voids. Both crystal growth and/or water absorption pressures may have caused cracking. (2) Void-fill and void-rim ettringite in larger interstitial pores and entrainment voids also cause loss of void effectiveness in preventing freezing damage when the concrete is water saturated.

We believe that the close association of ettringite with expansion cracks is evidence that the cracks were caused by ettringite growth. Our experimental production of concrete deterioration by sulfate solutions [56] supports these conclusions. Experimental results showed that immersion in a sodium sulfate solution produced significant expansion of concrete blocks simultaneously with ettringite precipitation. The amount of expansion was closely related to the experimental conditions. The greatest expansion occurred in concrete subjected to wet/dry cycles. Freeze/thaw conditions produced less expansion, and continuous immersion resulted in the least expansion. It was also observed that the presence of a crystallization inhibitor, such as diethylenetriaminepenta(miethylenephosphonic acid), prevented both expansion and new ettringite formation, almost certain proof that ettringite caused the expansion [56]. These observations indicate that different physical conditions are very important factors in the deterioration mechanism caused by ettringite formation. Under continuous immersion conditions, crystal growth of newly formed ettringite is the only available expansion mechanism. Expansion by crystal growth alone appeared to cause the least damage in concrete, as indicated by the relatively small amount of expansion resulting from continuous immersion. The fact that most expansion occurred during wet/dry cycling suggests that swelling by water absorption during wet/dry cycles, in addition to crystal growth pressure, is a major cause of damage. Under freeze and thaw experiments, both crystal growth pressure and void-fill/void-rim ettringite in larger interstitial pores and entrainment voids caused the loss of void effectiveness in preventing freezing damage under water-saturated conditions. Therefore, freeze-related cracking, which also results in concrete expansion, may occur. In conclusion, the experimental results document that Iowa highway concrete damage by ettringite expansion is accelerated with alternating wet/dry and freeze/thaw cycles.

6. Conclusions

Petrographic microscope and scanning electron microscopy, combined with EDAX area element mapping, document that delayed or secondary ettringite has an important role in the premature cracking of several Iowa highway concretes. Part of the evidence for this conclusion is the spatial association of ettringite with microcracks in the paste. The formation of the observed ettringite is related to the partial oxidation of pyrite inclusions in carbonate coarse aggregates. The oxidation of pyrite inclusions in the coarse aggregate appears to be sufficient to increase sulfur content above that originally present in the cement blends and to facilitate DEF reactions. Whether sulfate caused by pyrite oxidation results in all of the observed ettringite is uncertain because some ettringite crystals are not closely associated with oxidized pyrite masses. External sources such as contamination by sulfate minerals of deicer salts may account for part of the ettringite produced.

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