Sulfate Attack on Concrete Pavements in Mississippi

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During the past 15 years, the Testing Division of the Mississippi State Highway Department has observed and attempted to determine the causes of deterioration of concrete on some sections of highways within the state. Originally, it was believed that the deterioration was the result of physical causes, such as excessive finishing, overstressing, and lack of or improper placing of load transfer devices at joints. The deterioration consists of a gradual development of map cracking, discoloration in the area of the cracks, later scaling of the top surface, and eventual disintegration of the entire depth of the concrete in some cases. The phenomenon normally appears at joints and cracks.

Recently it was suspected that sulfate reaction may be a contributing factor in this deterioration. Suspicion was aroused when a concrete pavement was removed during new construction in an area where the presence of large amounts of sulfates was known to exist in the native surrounding soil. Tests and investigations confirmed the belief that these sulfates, transported by surface water, combined with the tricalcium aluminate in the portland cement used in the concrete to produce calcium sulfoaluminate crystals (ettringite). These crystals then grow in volume, resulting in overstressing and disintegration of the concrete.

As a result of this finding, the Testing Division has intensified its efforts toward an investigation of concrete deterioration resulting from sulfate attack. Various concrete pavements and some concrete parking lots in widely separated areas of the state have been and are being examined for evidence of sulfate attack. Results of these studies are reported in this paper.

•FOR THE PAST 15 yr, the Testing Division of the Mississippi State Highway Department has been observing concrete pavements which have developed a condition now well established as being at least partially due to a reaction of waterborne sulfates with portland cement. The theory of this reaction, in simplest terms, is that waterborne sulfates from surrounding and possibly underlying soils, react with the tricalcium aluminate (C_3A) in the cement to form calcium sulfoaluminate (ettringite). On evaporation of the water, this chemical deposits crystals which grow in volume with repeated depositions, eventually disrupting the concrete by overstressing. The attack always begins at a joint or at a crack in the concrete and, generally, at the intersection of a longitudinal and a transverse joint.

Disruption of the concrete in the form of surface crazing or map cracking usually appears within 7 or 8 yr after construction. The concrete adjacent to these cracks becomes discolored with a dark-colored exudation which gradually turns light gray (Fig. 1). The cracking increases and spreads until the upper portion of the concrete

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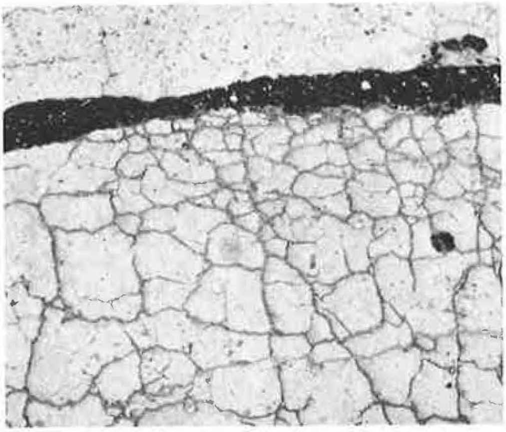

Figure 1. Typical appearance of intermediate stage of sulfate reaction in concrete.

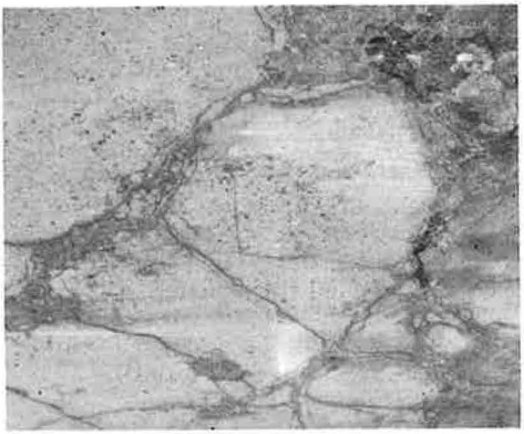

Figure 2. Close-up of cracking and spalling of concrete subjected to sulfate reaction.

separates from the lower portion and eventually spalls off (Fig. 2). It is believed that the original disruption occurs at the surface due to the more rapid evaporation of moisture from this area. The disintegration apparently progresses downward with time, finally resulting in disruption of the entire depth of concrete.

This phenomenon at first was believed to be caused by one or more or the following: excess finishing, improperly placed reinforcing steel or dowel bars, and concentrations of stresses due to other faulty joint construction. Before our first observation of the phenomenon, other states and agencies were experiencing alkali-silica reaction in concrete. At that time, the Testing Division explored this possibility in connection with our concretes and determined that, with one or two exceptions in the extreme northeastern portion of the state, concrete made with Mississippi aggregates is not susceptible to serious alkali-silica reaction. Aggregates used in the pavements discussed in this paper did not originate in the northeastern part of the state. It is our belief, therefore, that the deterioration of these pavements is not due to alkali-silica reaction.

These conditions first appeared on US 49, just north of Jackson, Miss. Cracking and discoloration were noted but were not considered serious at that time. The pavement was partly removed due to new construction and a portion was covered with asphalt for use as a service road before the conditions had progressed to an advanced stage. No investigations were made, therefore, but the same early conditions prevailed as on pavements later investigated.

It was only recently that Mr. and Mrs. Bryant Mather, on being consulted by the Testing Division and furnished samples of concrete in the process of disintegration, advised that the phenomenon appeared to be caused by sulfate reaction. With their cooperation, investigations were intensified, resulting in a tentative conclusion that waterborne sulfates, combined with a high C_3A content in the cement, constitute the primary contributing cause of the disintegration.

GENERAL DATA

Four sections of Mississippi highways exhibiting the foregoing conditions have been investigated and are discussed here. These four sections were constructed with the following common features: normal steel wire mesh reinforcement, formed longitudinal and transverse joints, load transfer dowels at all transverse joints, Type I cement, and a cement factor of 1.45 barrels/cu yd of concrete. Features not common to the four sections are given in Table 1.

At the time of construction of the projects studied, there were no specified requirements for aluminum oxide (Al_2O_3) or ferric oxide (Fe_2O_3) in Type I cement and no requirement for C_3A, a function of the two oxides. Consequently, the commercial laboratories testing the cement did not determine these values. Fortunately, however, for the purpose of this study, the cement companies did make such determinations and maintained complete records. During the investigation into possible sulfate reaction, the companies that produced cement for the four projects furnished, at our request, the analyses of the cement (Table 2). The values shown for each project and used in the following discussion are pertinent for the year during which shipments of cement were made.

PWA 75 AND PWA 327A, CHICKASAW COUNTY

During 1950, the author and A. R. Brickler of the Portland Cement Association made a detailed survey of this project, located in Chickasaw County, on Miss. 15, south of Houston. At the time of this survey, a large number of the interior corners (intersection of longitudinal and transverse joints) in the central portion of this project displayed distinct signs of distress in the form of broken and spalled concrete. There was some indication of distress at a number of transverse joints between the center and the edge of the slab. Tentatively, it was concluded from this survey that the distress was caused by either excess finishing, improper alignment of the steel dowels, otherwise faulty joint construction, or a combination of some or all of these factors. Since 1950, the disruption has advanced greatly.

As will be noted from Table 1, this 25-yr-old pavement was paved with two brands of cement: the south 2.75 mi and the north 3.57 mi with Brand B, the center 4.72 mi with Brand A(1). All other factors were the same (Fig. 3). According to the data furnished by the cement companies (Table 2), at the time of production for this project Brand A(1) contained an average of 17.2 percent C_3A; Brand B, an average of 11.3 percent. (Whenever a value for C_3A is stated here it is the calculated value.)

TABLE 1

CONSTRUCTION FEATURES FOR FOUR SECTIONS OF MISSISSIPPI HIGHWAYS INVESTIGATED FOR SULFATE REACTIONS

Project	County	Highway	Year Paved	Cross-Section	Length (mi)	Subgrade	Base Under Pavement	Curing Method	Location of Aggregate Source	Brand Cement Used	Joint Spacing (ft)		Wt Wire Mesh Reinforcing (lb/100 sq ft)	Avg. Strength	
											Expansion	Contr.		Beam[a]	Core[b]
PWA 75, 327A	Chickasaw	Miss. 15	1939	9, 6, 9 in. × 20 ft	11.04	Porters Creek	15 in. A2	Cotton mats	Near Columbus	A(1), B	40	None	53	872	6,304
F1(5), F32(4) U32(5)	Lee, Itawamba	US 78	1948	8, 6, 8 in. × 22 ft	13.68	Coffee sand and Mooreville chalk	15 in. A2	Paper	Columbus	A(1), B, C, D, E	—[c]	20½	39	815	6,007
UI-251(7)	Lauderdale	US 80	1949	8 in. uniform × 24 ft	6.16	Zilpha, Winona, Tallahatta formations	12 in. A2	Paper	Hattiesburg	A(1)	—[c]	31⅓	39	886	5,325
PWS 50A	Issaquena	US 61	1938	9, 6, 9 in. × 20 ft	6.99	Sharkey clay	None	Cotton mats	Claiborne County	A(2)	90	30	53	821	6,323

[a]Flexural, at 28 days.
[b]Compressive; at variable ages, all more than 28 days.
[c]Expansion joints spaced according to air temperature; none placed if temperature was 70 deg or above.

TABLE 2

VALUES FOR CEMENT USED IN PAVING MISSISSIPPI HIGHWAYS INCLUDED IN STUDY

Brand Symbol	Year	Yearly Avg. Percentage				Project Furnished
		Al_2O_3	Fe_2O_3	C_3A	C_4AF	
A(1)	1938	8.4	3.3	16.7	10.0	–
	1939	8.4	3.0	17.2	9.1	PWA 75, 327A
	1948	7.5	3.8	13.5	11.6	F1(5), F32(4), U32(5)
	1949	7.2	3.9	12.5	11.9	UI-251(7)
A(2)	1938	6.3	2.6	12.3	7.9	PWS 50A
B	1939	5.8	2.4	11.3	7.3	PWA 75, 327A
	1948	5.2	2.4	9.7	7.3	F1(5), F32(4), U32(5)
C	1948	5.7	2.3	11.2	7.0	F1(5), F32(4), U32(5)
D	1948	5.8	3.3	9.8	10.0	F1(5), F32(4), U32(5)
E	1948	6.3	2.4	12.6	7.3	F1(5), F32(4), U32(5)

In August 1964, a second detailed survey was made; in the section paved with Brand A(1) cement, it was noted that almost every transverse joint was seriously broken and spalled with the spalled area in most cases extending several feet from the joint. In numerous places the area adjacent to the longitudinal joint, between transverse joints, was badly spalled. Figure 4 is a typical example of the conditions existing on this section of highway.

In the two sections paved with Brand B cement, these conditions do not exist; the concrete shows only the normal signs of age, with one exception between stations 455 and 470 (approximate), a distance of about 1,500 ft or a normal day's run at that time. The conditions here are the same as in the Brand A(1) section. The reason for this exception has not been determined. At the time of paving the project, cement was in somewhat short supply and a different cement may have been used on the day that this section was paved, though records do not reveal such change.

Cores were drilled recently from this pavement, in both good and bad areas. Figure 5 shows typical examples of the condition of the concrete. An examination of the cores obtained shows the following:

1. Station 463 + 55 (in the 1,500-ft section of distressed concrete made from Brand B cement, according to our records)—concrete contains an abundance of ettringite, some gel and indication of frost damage, all suggesting the possibility of minor alkali-silica reaction as a result of previous cracking of the concrete;
2. Station 518 + 75 (Brand B cement, concrete in good condition)—concrete contains some gel and ettringite; and
3. Station 364 + 09 (Brand A(1) cement, concrete spalled and broken badly)—concrete contains a considerable amount of ettringite and some gel; a large amount of calcite is present in surface cracks.

This project lies in the Porters Creek formation, with all embankments and cuts consisting of this type of soil. Porters Creek clay is a dark gray, blocky, shaly clay, slightly glauconitic and micaceous, containing gypsum crystals (calcium sulfate) and some marcasite nodules which weather rapidly to hydrated iron sulfate (melanterite). A sample of the soil from a typical cut contained 1.88 percent soluble sulfate (as determined by U.S. Army Corps of Engineers Test Method CRD-C403-59) and had a pH of 3.1 (Table 3). Approximately 15 in. of fair quality sand clay were placed as a base under the concrete pavement.

F1(5), F32(4), U32(5)—LEE AND ITAWAMBA COUNTIES

In Lee and Itawamba Counties, on US 78, east of Tupelo, is a concrete highway paved in 1948. Several years after the highway was paved, the concrete in various parts of the project was showing signs of deterioration. Alkali-silica reaction was again suspected. However, the aggregates were obtained from the Columbus, Miss. area and these are definitely not alkali-reactive aggregates.

This pavement was placed during a time period when portland cement was in short

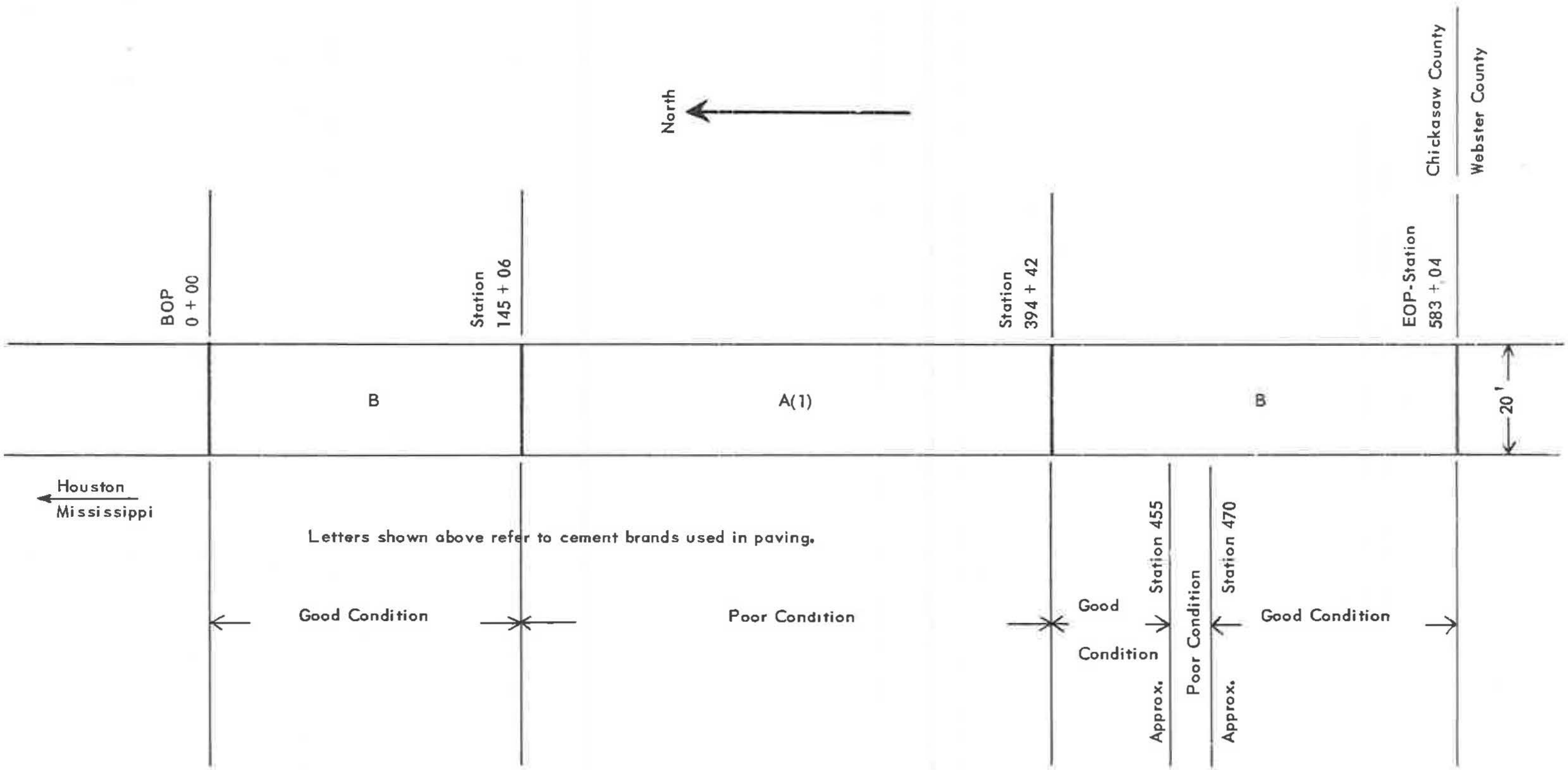

Figure 3. Project PWA 75 and 327A, Chickasaw County, Miss. 15.

TABLE 3

SOLUBLE SULFATES AND pH IN SOILS ADJACENT TO SECTIONS OF MISSISSIPPI HIGHWAYS INVESTIGATED

Project	County	Sol. Sulfates[a] (%)	pH
PWA 75, 327A	Chickasaw	1.88	3.1
F1(5), F32(4), U32(5)	Lee, Itawamba	0.55[b]	2.9
		0.33[c]	7.2
PWS 50A	Issaquena	0.43	5.0
UI-251(7)	Lauderdale	0.45	4.6

[a]Corps of Engineers Method CRD-C403-59.
[b]Mooreville chalk in eastern portion.
[c]Coffee sand in western portion.

Figure 4. Typical view of 25-yr-old concrete pavement on project PWA 75 and 327A, Miss. 15, showing patching at transverse joint and spalling at left; two cores previously drilled from area.

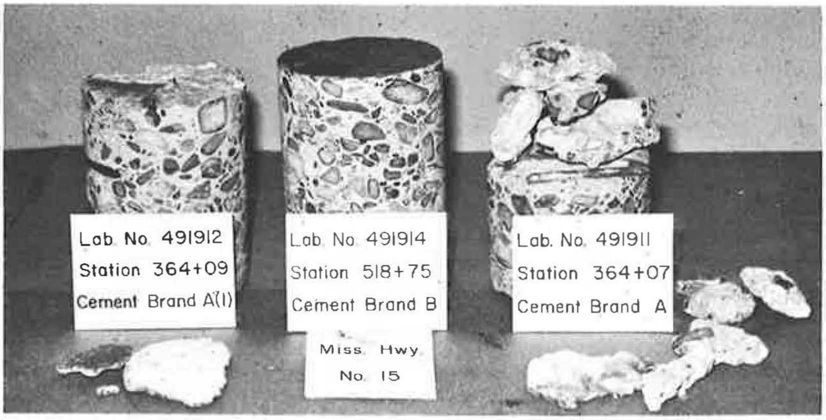

Figure 5. Cores drilled from Project 75 and 327A, Miss. 15; concrete in cores on left and right made from cement Brand A(1), center core from Brand B.

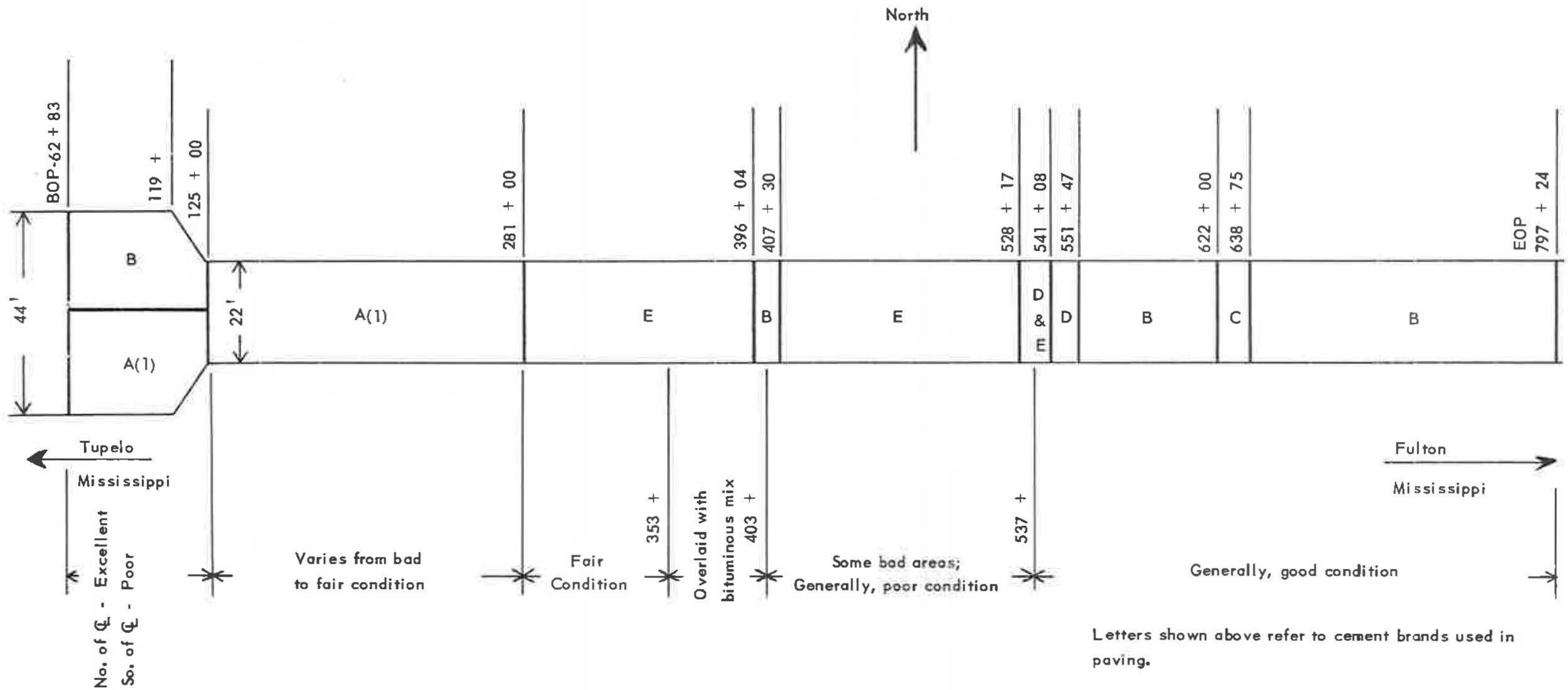

Figure 6. Project F1(5), F32(4), U32(5), Lee and Itawamba Counties, US 78.

Figure 7. Project F1(5), 32(4), U32(5), US 78, facing west; concrete on right of centerline made from Brand B cement, on left from Brand A(1) cement; pavement age 16 yrs.

supply and, consequently, several brands of cement were used intermittently in the construction as shown in Figure 6.

Recently, it was discovered that in those sections in which Brands A(1) and E were used, the concrete is in bad condition, generally, with the same symptoms described earlier in this paper. It will be noted that cement Brand A(1) had an average C_3A content of 13.5 percent; Brand B, 9.7 percent; Brand C, 11.2 percent; Brand D, 9.8 percent; and Brand E, 12.6 percent. The cements in the concrete now showing distress were the two with the highest C_3A content, both in excess of 12 percent.

A spectacular example of contrasting conditions exists from station 62 + 83 to station 125. In this section, as shown in Figure 6, Brand B cement was used in the westbound lane and Brand A(1) in the eastbound lane. The former shows no deterioration, whereas every transverse joint in the eastbound lane exhibits advanced symptoms of sulfate reaction (Figs. 7 and 8). The difference cannot be attributed to traffic since reliable information indicates that the westbound lane has been subjected to very much heavier wheel loads by the hauling of gravel to Tupelo and projects to the west. Where Brand E was used, the distressed areas are somewhat intermittent; Figure 6 indicates that nearly 1 mi of Brand E cement concrete has been covered with a bituminous overlay because of the poor condition of the concrete.

Cores were drilled recently from the

Figure 8. Project F1(5), 32(4), U32(5), US 78; view of transverse joint, facing north; concrete in foreground from Brand A(1) cement, beyond centerline from Brand B; typical of joints in widened portion of project; pavement age 16 yrs.

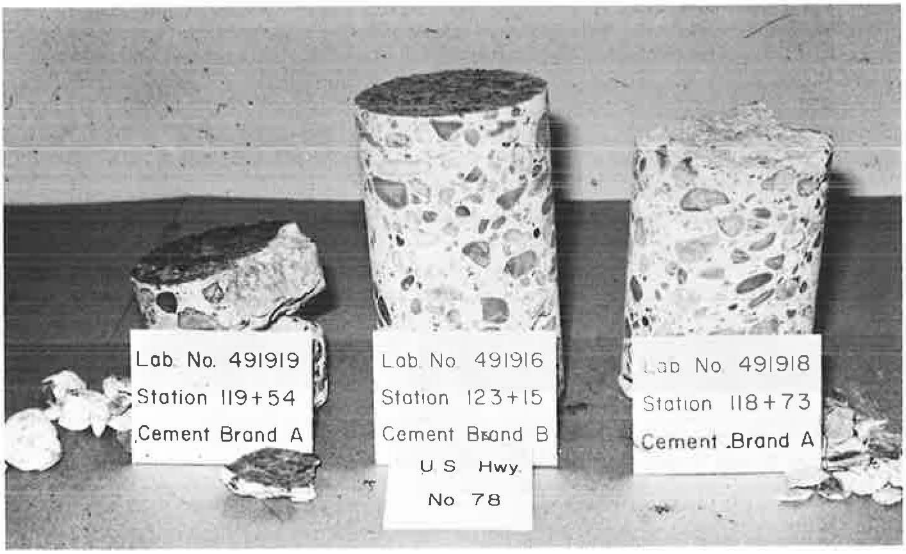

Figure 9. Project F1(5), F32(4), U32(5), US 78; cores on right and left represent concrete made from Brand A(1) cement, in middle from Brand B.

concrete at various locations. Figure 9 shows typical examples of the condition of the concrete at this time. Examinations of these cores reveal the following:

1. Station 123 + 15 (Brand B cement; pavement in good condition)—concrete contains a very small amount of gel and ettringite;
2. Station 118 + 73 (Brand A(1) cement, pavement badly broken)—concrete contains a large amount of ettringite and shows cracking, top and bottom of the core, parallel to the surface; and
3. Station 407 + 57 (Brand E cement, concrete in a short section of distressed pavement)—concrete contains more ettringite than that at station 123 + 15, but less than that at station 118 + 73.

Most of the natural soils within the limits of the project have a very high sulfate content. Predominantly, these soils are Coffee sands and Mooreville chalk. The Coffee sand formation is a light gray color, crossbedded to massive glauconitic sand and sandy clay, containing some calcareous sandstone. Numerous nodules of marcasite are present in this soil in the Tupelo area. Mooreville chalk is a marly chalk and calcareous clay. In some areas this is a dark, shaly type of clay, containing considerable quantities of melanterite.

Samples of the natural soils were obtained from cutbanks, source of the embankment materials. The west end of the project is in the Coffee sand formation, which contains 0.33 percent soluble sulfates; the east end is in the Mooreville chalk series, which contains 0.55 percent soluble sulfates; pH values are 7.2 and 2.9, respectively (Table 3). It is our belief that the sulfates in these soils, combined with the high C_3A content of cement Brands A(1) and E, have been the primary cause of the deterioration of this pavement.

Figure 10 is a photograph of the Mooreville chalk taken at the base of a ditch backslope, after more than 16 yrs. of exposure.

The concrete pavement from the east end of this project to the Alabama state line is several years older than the preceding project. It is showing advanced deterioration also, but the appearance and type of disruption is entirely different from that caused by sulfates. Aggregates were from an area which has been excluded for several years by the Mississippi State Highway Department from use in concrete due to

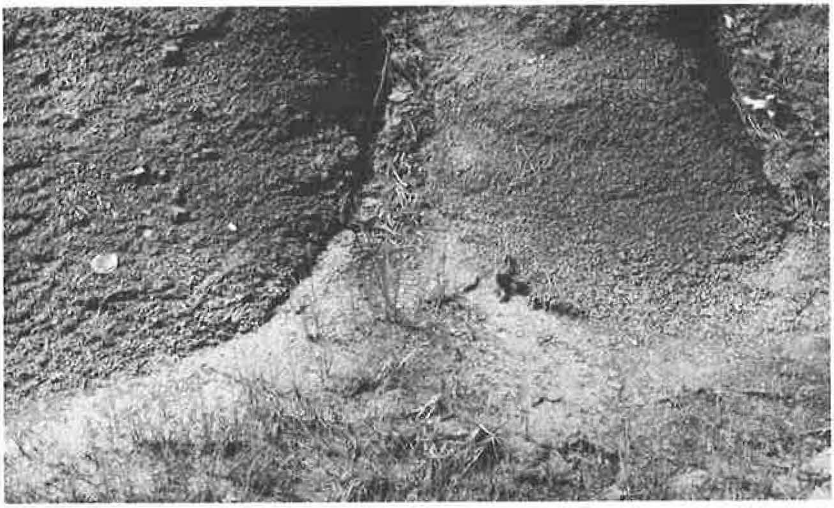

Figure 10. Project F1(5), 32(4), U32(5), US 78; typical appearance of Mooreville chalk in backslope of ditch after 16 yr of exposure (note scant vegetation).

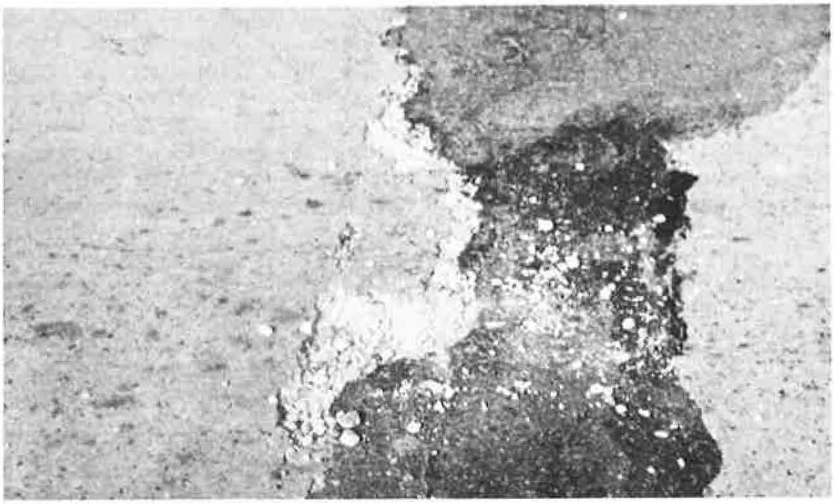

Figure 11. Project PWS 50A, US 61; close-up of concrete attacked by sulfates showing patched and spalled areas, typical of transverse joints on this project; pavement age 26 yr.

the presence of opal, as determined by petrographic examination. The concrete contains an abundance of gel but little or no ettringite. This is probably one of the few cases of alkali-silica reaction in Mississippi.

PWS 50A, ISSAQUENA COUNTY

This pavement, in Issaquena County on US 61, was constructed in the summer of 1938. During the study of sulfate reaction, it was reported that the pavement exhibited the same conditions as the other pavements studied. An inspection revealed that this is apparently another case of sulfates reacting with the cement. Figure 11 shows a typical condition of this pavement. Cement Brand A(2) was used on this project; the cement contained an average of 12.3 percent C_3A.

Samples of the surface concrete were obtained from a spalled area. Examination of these samples shows thorough deterioration and the presence of large amounts of ettringite. This project lies in the floodplains of the Mississippi River, in an area containing soils usually referred to as "delta gumbo." The water table in the area is high. The soils contain considerable organic material and a large percentage of soluble sulfates; a sample of the soil from beneath the edge of the slab contained 0.43 percent with a pH value of 5.0 (Table 3). Cores of the soil, taken at depths of 3 to 20 ft, were found to contain a very large quantity of gypsum and iron sulfate. The greatest concentration of these chemicals is in the upper 3 to 5 ft.

UI-251(7), LAUDERDALE COUNTY

In 1949, US 80 was relocated west of Meridian, Miss. The original concrete paved highway, a narrow, winding road traversing the higher ridges in this area, has exhibited no symptoms of any reaction. The pavement on the relocation, however, began to show signs of deterioration at the age of about 7 yr. As this deterioration was rapidly becoming worse, an investigation was started in 1957 to determine the cause. Later, in 1962, it was necessary to remove a badly disrupted portion of the pavement to make a connection with I-20 then under construction. It was possible, therefore, to examine the concrete without being limited to small samplings as with cores.

It was in connection with this project that Bryant and Katherine Mather were first consulted. After examination of several pieces of concrete, they tentatively concluded that the conditions were caused by sulfate reaction. However, they more probably result from a combination of causes and an acceleration of effect; the areas surrounding this project have a very high acid content, as well as a high sulfate content. A sample of soil obtained from a cut on this project contained 0.45 percent of soluble sulfate and a pH value of 4.6 (Table 3). Figures 12 and 13 show typical conditions of the pavement on this project. Cement Brand A(1) used in the concrete contained an average of 12.5 percent C_3A.

Figure 14 shows the typical condition of cores drilled from this pavement. Examination of the cores and the samples obtained during the removal of the pavement indicates the presence of large amounts of ettringite. The cores were badly broken with numerous cracks parallel to the surface at various depths. Some of these cracks extended almost entirely around the periphery of the core.

This project lies principally in the Zilpha and Tallahatta formations. Zilpha clay is a chocolate color and contains some glauconite, large amounts of marcasite and considerable gypsum, which weathers very rapidly to melanterite. Tallahatta clay is a glauconitic clay and siltstone with lenses of sand and some sandstone, highly cross-bedded, blocky, with numerous joints throughout. Tallahatta clay also contains considerable lenses of marcasite, as well as elemental sulfur. Figure 15 is a typical view of a cutbank in the vicinity of this project.

Mineralogy studies of soils submitted to and examined by Katherine Mather confirm the presence of varying amounts of gypsum, unstable pyrite, jarosite ($KFe_3(SO_4)_2(OH)_6$) and siderotil ($FeSO_4 \cdot 4H_2O$) (1). These are probably the immediate sources of sulfates.

Three samples of deteriorated concrete obtained from this project by the Testing Division were submitted to the U.S. Army Engineer Waterways Experiment Station at Jackson, Miss. These included a fragment of concrete (Sample A) and two drilled cores (Samples 7 and 8).

The samples of concrete were analyzed chemically to determine whether the sulfate content of the concrete (and, therefore, of the cement) had increased over the amount previously present. These analyses were made in accordance with a test method currently being considered by ASTM Committee C-9, Subcommittee III-1, and described in the Appendix. Calculated results of the tests are given in Table 4.

It was the original intention to confine this study principally to the physical and geological aspects. The limited chemistry on the concrete (Table 4) is admittedly far from adequate; the need is recognized for considerably more chemistry before more confidence can be placed in the results. In addition, one should take into account the variations inherent in field proportioning of concrete and the normal errors of testing.

Figure 12. General view of US 80; project UI-251(7), showing effects of sulfate reaction; pavement age 15 yr.

Figure 13. Close-up of transverse joint on project UI-251(7), US 80; pavement age 15 yr.

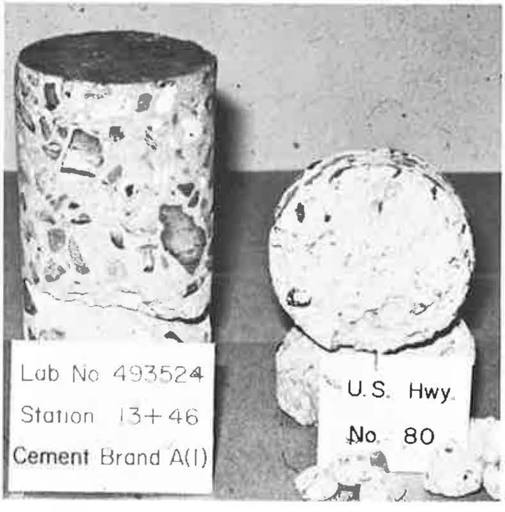

Figure 14. Two cores drilled from concrete pavement on US 80, project UI-251(7); concrete in both cores made from Brand A(1) cement.

Although the three specimens tested were obtained from distressed concrete on the same project, the test results are at considerable variance. Sample A shows a significant increase in SO_3 from that in the original cement but little or no decrease in cement content; Samples 7 and 8 show the opposite, i. e., little or no

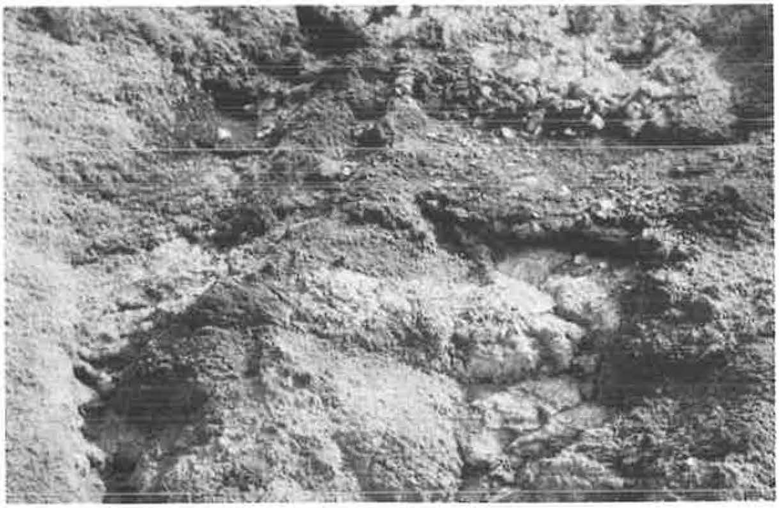

Figure 15. Project UI-251(7), US 80; typical appearance of Zilpha clay in cutbank, showing lack of vegetation and light-colored areas with covering of melanterite.

TABLE 4

CALCULATED RESULTS OF DETERMINATIONS OF CEMENT AND SULFATE CONTENT OF SAMPLES OF DETERIORATED CONCRETE[a]

Determination	Value		
	Sample A	Sample 7	Sample 8
Type of sample	Fragment	Core	Core
Condition of concrete	Fair	_[b]	_[b]
Cement content (oven-dried wt, (550 C))	14.43	12.44	13.53
% SO_3			
In cement in concrete	2.14	2.04	1.97
In original cement[c]	1.98	1.98	1.98
Increase in SO_3 (%)	0.16	0.06	-0.01
Cement as received			
% in concrete	13.75	11.91	13.03
Lb./cu yd	531.0	460.7	500.1
Sk/cu yd	5.6	4.9	5.3
Sk/cu yd cement originally incorporated, theoretical	5.8	5.8	5.8
Loss cement from original (sk/cu yd)	0.2	0.9	0.5

[a]Brand A(1) cement used; from project UI-251(7) in Lauderdale County; results as reported by Leonard Pepper, Chief Chemist, U.S. Army Waterways Experiment Station, Jackson, Miss.

[b]Extremely poor condition, broken, and cracked on top and bottom of core parallel to pavement surface.

[c]From average cement analysis during period between May 27 and Sept. 17. 1949.

increase in SO_3 but a possible decrease in cement content. There are no apparent reasons for these variations; however, they possibly occurred because the test method requires a minimum sample of 10 lb; the samples as submitted each weighed approximately this amount and, therefore, the whole sample was tested, the results representing the average analysis of all the concrete in the sample. The amount of affected and deteriorated concrete represented a very small portion of the whole sample, and it was realized after completion of the tests that the analysis should have been made only on this small portion. This procedure probably would have given a more accurate indication of chemical changes in the concrete.

Samples 7 and 8, it will be noted, indicate decreases of 0.9 and 0.5 sk/cu yd, respectively, in cement content from that theoretically in the original concrete. These decreases are considered to indicate losses of cement which resulted from leaching of the calcium in the cement; this would, in turn, indicate the movement of foreign water through the concrete.

The chemical results tend to support the theory that the deterioration of the concrete pavement, on this project in particular, is due to a combination of chemical reactions, with two probable reactors being the acids and sulfates from the surrounding soils reacting with certain components in the cement.

SUMMARY AND CONCLUSION

For sulfate reaction to take place, certain factors must be present; namely, soluble sulfates, water to dissolve and transport the sulfates, C_3A in the cement, and evaporation of water from the surface of the concrete. It is believed that a reaction takes place if these factors exist to any degree but that the speed and intensity of the reaction varies directly with an increase in any factor; that is, if either is limited, the reaction can be delayed or rendered innocuous.

It is impractical to cover a new concrete pavement to reduce evaporation of water; however, this appears to be a possible deterrent to further reaction on old concrete under sulfate attack. Limitation of C_3A to a low percentage appears to be the most practical means of preventing or delaying the reaction.

AASHO Standard Specification M 85-60 limits C_3A content for Type I cement to 15 percent; before 1960 there was no such limitation. In Type II cement it is limited to 8 percent; in Type III to 15 percent, except that the engineer may specify a maximum of 8 percent for moderate sulfate resistance or a maximum of 5 percent when high sulfate resistance is required; Type V cement is limited to 5 percent C_3A. Thus, there are safeguards provided by AASHO standards, and it becomes the responsibility of the engineer to determine the type of cement best suited to the existing conditions.

An interesting observation from this limited study has been that concretes containing cement with C_3A content less than 12 percent have exhibited to date no serious sulfate reaction, whereas those with more than 12 percent have deteriorated, apparently as a result of sulfate reaction. Cook, in commenting on a research project on which, in 1940, concrete specimens were cast from 51 different cements and exposed to seawater at Salt Run, St. Augustine, Fla., states (2): "After nine years a total of only nine of the specimens had failed; eight of these specimens contained one or the other of the only three cements among the fifty-one used that had a calculated tricalcium aluminate content greater than 12 per cent."

On the projects in Chickasaw, Lee and Itawamba Counties, we obtained samples of the underlying soils through the core holes drilled in the pavement. In all cases, chemical analysis showed that these soils contained only a trace (0.01 percent or less) of soluble sulfate, although the subgrade soils contained from 0.33 to 1.88 percent. A somewhat granular topping material was placed under these pavements. On the Issaquena County project, the soil directly under the pavement consisted of Sharkey clay with 0.43 percent soluble sulfate; no granular material was placed under the concrete.

As an explanation of the reason for the low sulfate content of the granular subsoils, it has been suggested that the water, carrying sulfates obtained from the surrounding soils, loses only a minute amount of sulfate in traveling through granular soils under the pavement due to the chemically inert nature of these soils, and that the greater portion of the sulfates is deposited in the concrete because of the chemical nature of the concrete. Another suggestion has been made that some of the sulfates are carried by surface water and deposited in cracks by gravity, a small amount gravitating into the underlying soils. Either suggestion may be an explanation of the low sulfate content of the soils under the pavement.

A cement-treated base, whether under an asphaltic or a concrete pavement, is effectively sealed by the pavement, and evaporation of water from the surface of the base is eliminated. Since surface drainage is today recognized as a major design factor, the possible problem of surface water delivering sulfates to the surface of the pavement should be minimized. Therefore, now that we are aware of the existing problem, we feel that steps have been and are being taken to prevent any major recurrence of the disruption of pavements described in this paper.

Mississippi is, and has been for some time, cement treating all bases under asphalt or concrete pavements and usually places a granular subbase under the treated base. These two insulating layers should effectively reduce any reaction from sulfates except in those areas of abnormally high acidity or sulfate-bearing soils. In such areas, Type II cement, or Type I with a maximum C_3A content of 8 percent, is being required both in the cement-treated base and in the paving concrete.

Although results of our studies indicate that cement Brands A(1), A(2) or E have been used in the affected areas, it is not the purpose of this paper to condemn these or any other brand or any source of portland cement. The cement furnished the projects described was tested and inspected by reputable commercial laboratories and the cement complied with the specifications prevailing at the time of construction.

In addition to the sections of pavement described, there are other areas in Mississippi in which the concrete pavements exhibit symptoms of possible sulfate reaction. This paper includes only those actually studied and investigated. However, it is not the intent to convey the impression that all concrete pavements in Mississippi are defective. Actually, the sections noticeably affected by what appears to be sulfate reaction constitute only a small percentage of Mississippi concrete highways. Each section described in this paper has served, or will continue to serve, satisfactorily during a normal and expected life-span. Some sections have been overlaid with an asphaltic pavement; such an overlay, maintained properly and sealed from time to time to prevent or reduce evaporation of water, will act as a deterrent to further deterioration of the concrete.

A word of caution may be appropriate. After studying the sections of concrete pavement, we have perhaps become sulfate reactivity conscious. Recently, a few small areas were noticed in a new concrete pavement that resembled the beginning of sulfate reaction deterioration. Samples of the concrete showed the presence of a small amount of ettringite and immediately it was concluded that perhaps we had a case of accelerated sulfate reaction. On removal of the defective concrete and a study of the placing records, however, it was determined that the trouble resulted from physical causes. Sulfate reaction, therefore, is not always the cause of trouble.

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Appendix

METHOD FOR DETERMINATION OF CEMENT AND SULFATE CONTENT IN HARDENED CONCRETE

This method follows the procedures in a test method under consideration by the ASTM Committee C-9, Subcommittee III-1:

1. Sample is broken into 2- to 3-in. particles and allowed to dry to constant weight at 105 C.
2. The particles are then heated for 3 hr at 550 C.
3. The aggregates in the heat-treated sample are cleaned by hand and by scraping with a spatula; the sample is separated into three sieve fractions—retained on the No. 4, passing the No. 4 and retained on the No. 20; passing the No. 20.
4. The individual fractions are weighed; the plus No. 4 and the No. 4 to No. 20 sieve fractions are washed with dilute HCl to remove adhering cement and reweighed.
5. A representative portion of the minus No. 20 sieve material is ground in a mortar and pestle to pass a No. 200 sieve; this material is used for all chemical determinations.
6. Weight losses at 105 and 550 C are recorded.

Before the samples are prepared in this manner for analysis, they are stored in water for 96 hr, weighed in water, and then weighed in air in a saturated surface-dry condition. These weights are obtained to convert cement content from percentage by weight to sacks per cubic yard.

Discussion

HOWARD NEWLON, Jr., and W. CULLEN SHERWOOD, Virginia Council of Highway Investigation and Research, Charlottesville, Va. —The interesting paper by Mr. Lossing focuses attention on the importance of providing proper safeguards against chemical attack of paving concrete in certain geographical areas and also points up the need to consider the inherent interrelationships between structural and materials behaviors. The cases cited by the author are similar in many respects to an 18-yr-old pavement near Fredericksburg, Va., that the writers have studied intermittently for several years in an attempt to explain its relatively poor performance.

Although no general problem of sulfate attack is known to exist in Virginia, there are sizable areas in which soluble sulfates are found. In addition to extensive seawater exposures, jarosite (4) and other soluble sulfates have been reported in the Coastal Plain area. In the Piedmont and Ridge and Valley portions of the state, sulfate sources include oxidation products of sulfides brought to the surface by mining of coal and metallic ores and the weathering of disseminated sulfides from schists and black shales. Sulfates from some limestones and from rather extensive evaporite deposits in the Saltville area of southwest Virginia might also be of local concern. Because of these areas, Type II cement has been required by the Virginia Department of Highways for all structural and paving concrete since its introduction. This requirement has tended to alleviate or strongly reduce problems of chemical durability which might otherwise exist.

The project that the writers have studied, although small, is of particular interest since it was an experimental pavement embodying different structural designs of varying joint spacing and reinforcement. Thus, it is important in diagnosing the observed

TABLE 5

VARIATIONS OF CEMENT COMPOSITION FROM PROJECT TEST REPORTS

Cement	C_3A (%)	C_3S (%)	SO_3 (%)	MgO (%)
A	6-8	38-49	1.28-1.75	1.29-1.56
B	7	39-47	1.50-1.82	2.51-2.65
C	5-8	39-44	1.81-2.00	2.91-3.20

Figure 16. Views of project showing type of distress associated with concrete (cement C), with lane on far site of median showing no distress (cement A).

failures to isolate as much as possible the effects of structural design from other factors such as chemical attack. In the interest of brevity, details of the project will be omitted here, although they are available in several unpublished reports (e.g., 6, 7). It is sufficient to say that normal materials and construction procedures were used.

During the progress of the work three different cements were used; some of the important characteristics are given in Table 5. It will be noted that the cements were all similar Type II's, except for the MgO content which was relatively high in cement C.

Although the performance of the concrete was obviously influenced by the variations in structural design and conditions of drainage, there were also differences in performance that appear to be related to the cements used. Performance was generally poor in concrete made with cement C, intermediate for that with cement B, and good with cement A. Poor performance became extensive in portions of the concrete made with cement C when the pavement was 3 to 5 yr old. The concrete containing cement C has been resurfaced twice, that with cement B once, and that with cement A is still performing without resurfacing.

The behavior of the most affected concrete at an age of 6 yr is shown in Figures 16 and 17. The similarity to the behavior described by Mr. Lossing is apparent.

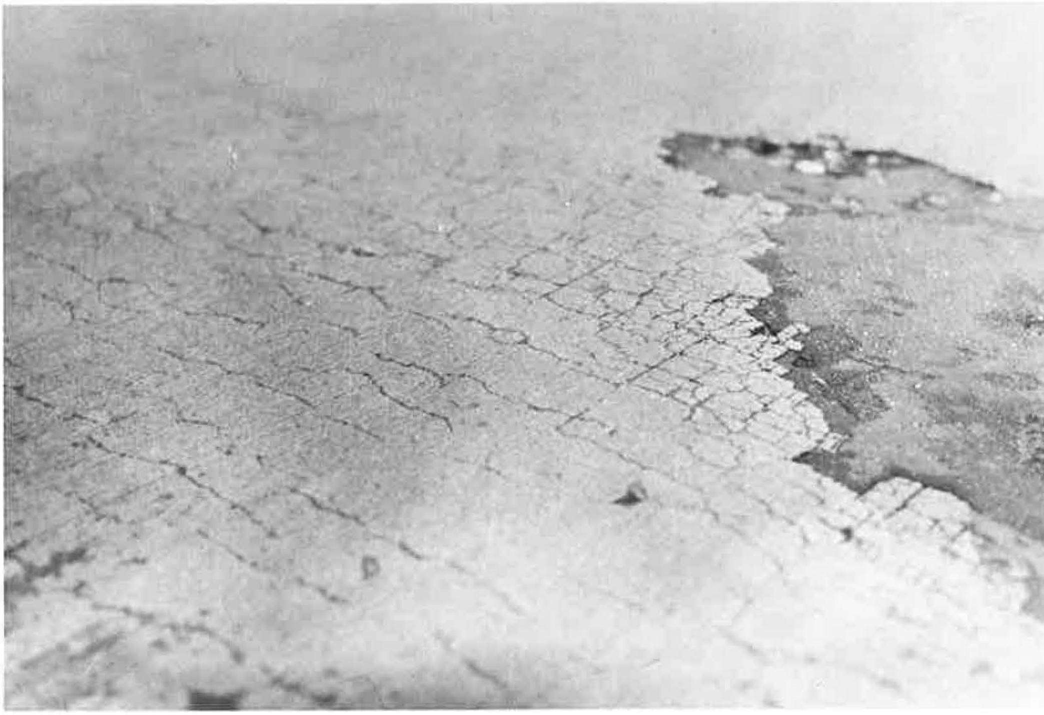

Figure 17. Close-up of distressed concrete from Figure 16.

Since the characteristics of the concrete suggested a mechanism other than structural failure, samples of the various concretes were taken for laboratory analysis. These samples showed extensive secondary deposits in voids and aggregate sockets. Figure 18 is a close-up of a fracture surface. Ettringite ($3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 31\,H_2O$) was found to constitute the major portion of the secondary deposits with measurable amounts of gypsum ($CaSO_4 \cdot 2\,H_2O$) and brucite ($Mg(OH)_2$) present. Although the finding of ettringite in deteriorated concrete is not uncommon, the presence of uncombined gypsum in the concrete was of particular interest as a possible indication of sulfate in excess of that attributable to the cement.

Uncombined gypsum of undetermined origin was reported by Mather and Mielenz in concrete from the McPherson Test Road (3). They concluded, however, that no sulfate attack had occurred since there was no addition of sulfate from the subgrade. On the basis of such literature and discussions with other workers in the field, the writers believed that it was necessary to demonstrate an amount of SO_3 in the concrete greater than would be attributed to the cement. Accordingly, samples of the concrete and the base material directly below the pavement were selected for analysis. Some analyses have been completed and more are in progress. On the basis of the results to date, it can be stated with reasonable certainty that the sulfate content of the distressed concrete is neither significantly greater than would be expected from the original cement nor higher than that found for the sound concrete. In fact, the reverse appears to be true. It is interesting to note that Mr. Lossing found essentially the same thing, including no sulfate in the base material, even though considerable sulfate existed in the surrounding soil.

To date it appears that study of the Fredericksburg pavement has brought forth evidence which may be interpreted both for and against sulfate attack. At the present time, the evidence indicative of sulfate attack may be summarized as follows:

1. Observed distress is the type expected from a chemical breakdown of the concrete as opposed to structural failure;

Figure 18. View of fractured concrete removed from the pavement shown in Figure 16, showing the white secondary deposits coating aggregate particle and socket and forming two small nodules shown in upper center.

2. Soluble sulfate minerals are known to occur in the area;
3. Soluble sulfates in amounts as great as 0.09 percent were indicated for the base material under the pavement and from the project borrow pit;
4. Large amounts of ettringite were found to be concentrated in voids and cracks and at the aggregate-mortar interface in the deteriorated concrete;
5. Small, but measurable, amounts of gypsum and brucite were detected in the ettringite by X-ray diffraction and microscopic examination;
6. Deterioration of the concrete appears to be related to the three brands of cement utilized in the project; and
7. Deteriorated concrete was limited to low areas of poor drainage where sulfate-bearing waters, if present, have ready access to the pavement.

Evidence indicating that sulfate attack may not have occurred is as follows:

1. Percentages of soluble sulfate in base material used immediately below the pavement (ranging from 0.024 to 0.093) are below 0.10 percent, often considered the minimum necessary for deleterious attack;
2. Sulfate contents of the concrete samples are generally lower than that added with the cement alone;
3. Sulfate contents in the deteriorated concrete were slightly lower than those in the sound concrete;
4. Sulfate contents in the base material under the distressed concrete are generally lower than those for material under sound concrete;
5. From project test reports and mill analysis, the average C_3A content of the concrete used in the deteriorated areas was lower (thus more resistant to attack) than that of the adjacent unaffected concrete;

6. X-ray diffraction patterns of the distressed concrete showed normal calcium aluminate hydrates that are usually broken down during sulfate attack to form calcium sulfoaluminate; and
7. Type II cement was used throughout the project.

Despite the seemingly conflicting evidence for and against sulfate attack, a few basic observations concerning the field concrete can be made. Certainly, the type of distress exhibited by the pavement was due to an instability within the material rather than to structural weakness. Whatever mechanism caused the cracks initially, it appears safe to assume that the presence of brucite and gypsum indicates some reaction between the original concrete constituents, predominantly $Ca(OH)_2$, and Mg^{++} and SO_4^{--} ions that occur in the ground water. Furthermore, the resulting volume increase accompanying formation of these reaction products and ettringite probably helped to widen existing cracks and contributed to the general distress.

The primary evidence suggesting that sulfate attack has not occurred is that the sulfate content of the concrete is not excessive and that the sulfate content of the base material is low. This situation, however, coincides with the experiences cited by Mr. Lossing where there is other strong evidence that sulfate attack has occurred. The inability to establish the presence of excess sulfate might result from a number of causes; for example, difficulties in obtaining a representative sample for analysis, removal of the sulfate from badly deteriorated concrete by percolating waters or by a mechanism involving resolution of the sulfate from the ettringite such as that described by Moum and Rosenqvist (5), or some other as yet unsuspected factors.

Thus, one is led to question seriously the necessity of clearly demonstrating an increase in sulfate content beyond that supplied with the cement in deteriorated concrete suspected of sulfate attack.

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