

Part II. APPLIED STUDIES

Alkali-Carbonate Reactivity—An Academic Or a Practical Problem

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The objective of this progress report of a study being conducted in Missouri is to present evidence indicating that alkali-carbonate reactivity is a practical rather than an academic problem.

Extensive expansion and cracking of some concretes have been associated with alkali-carbonate reactivity. Also, pursuance of this study has turned up evidence of alkali-silica reactivity.

Results of the prism test on more than 230 samples reveal that some rocks in Missouri are sufficiently reactive to cause concern.

Results obtained disclose that the chemical composition of reactive rock may differ appreciably from the previously suggested ranges of 40 to 60 percent dolomite in the carbonate fraction, and 10 to 20 percent acid insoluble.

No recommendations are made concerning acceptance or use of reactive rocks, but the need for such is recognized and the problem is discussed.

Suggested causes of the observed increase in occurrence and progression of the type of cracking in concrete attributed to alkali-aggregate reaction are presented.

•IN recent years considerable information (1, 2, 3) has been presented regarding the reactivity of some carbonate rocks with the alkali in portland cements. Despite this knowledge, there apparently is some question as to whether this is an academic or a practical problem. Apparent reasons for this situation are

1. Because of the recent recognition of this type of reactivity, little is known concerning the geographic and geological distribution of reactive carbonate rocks, or the extent to which this reactivity has affected or contributed to major failures of concrete pavements and structures; and
2. Some reactive carbonate rocks may have been considered above suspicion because their chemical composition differed from that reported to be characteristic of reactive rocks.

It is, therefore, the purpose of this progress report of a study under way in Missouri to present information indicating that this could be a practical problem wherever carbonate rocks are used in concretes.

INITIAL EVIDENCE OF THE PROBLEM IN MISSOURI

In the last 15 years, many requests have been received for approval of new sources of carbonate rock for concrete aggregate. This condition is a result of an increase in construction, depletion of rock at previously approved sources, and elimination of the use of gravels as coarse aggregate in PCC pavements. In 1953, samples of rock were received from one of these previously unapproved sources. The physical properties of this rock showed that it should be satisfactory for use as a concrete aggregate. This rock, however, was not only from a previously unapproved quarry, but was also from a previously unused geological formation. It was, therefore, decided to test the durability (frost resistance) of this rock in concrete.

In performing the freezing-and-thawing tests on concrete beams made with this rock, the initial length change measurements were made at 7 days and the second measurements were made at the end of the curing period (42 days). During this 35-day period the concrete containing this rock showed an unusual increase in length of 0.03 percent. This expansion was approximately one-third that (0.10 percent) considered by some investigators to be evidence of serious deterioration in freezing-and-thawing tests. Not only did this concrete expand during the curing period, but the 42-day flexural strength was at least 20 percent lower than anticipated. How much of this reduction in strength was due to the excessive expansion is unknown, but there is a fairly strong indication of a cause and effect relationship.

Companion specimens (3.5 × 4.5 × 16 in.) of those subjected to freezing and thawing were placed in an outdoor test pit (Fig. 1) at 7 days of age. Changes in dynamic modulus and length of this concrete and a concrete containing a chert gravel are shown in Figure 2. The total percent alkali (calculated as sodium oxide) was 0.73 and 0.66, respectively, for the cements used with the carbonate and chert aggregates. The results in Figure 2 show that the behavior of the concrete made with the partially saturated rock was radically different from that made with the vacuum-saturated gravel. The

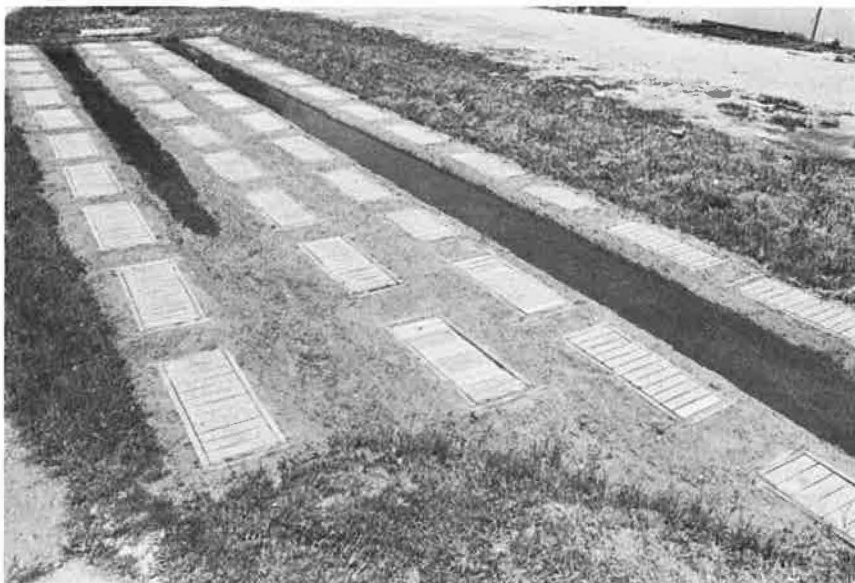


Figure 1. Concrete beams in outdoor test pit.

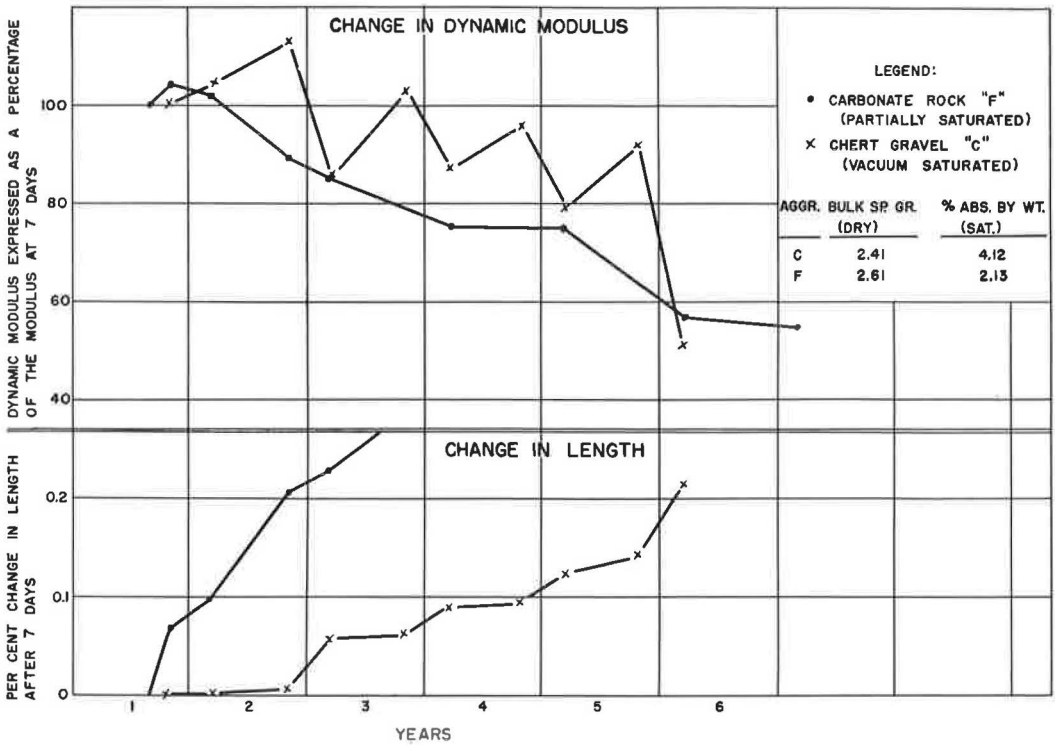


Figure 2. Normal concrete subjected to outdoor exposure.

deterioration of the concrete made with the gravel was obviously due to frost action, as shown by the fact that the loss in dynamic modulus and increase in length occurred primarily during the winter months (November to March). The concrete made with the rock, however, deteriorated throughout the entire year with an indication that the rate of deterioration was slightly greater from March to November, or during the period of non-frost action.

Examination of this rock revealed the presence of finely divided pyrite, and decomposition of the pyrite was considered as a possible cause of the expansion of the concrete. Subsequent tests, discussed later, revealed that the probable cause was alkali-carbonate reactivity.

As a result of the unexpected expansion of this concrete, this rock was not approved for use in portland cement concrete. It had, however, been used in local construction, and the behavior of the concrete believed to have been made with this aggregate is shown in Figure 3. The cracking in this panel of a sidewalk was of above average severity.

All panels of the sidewalk did not exhibit this cracking, and some panels were sound, giving evidence of variation in the factor or factors causing the deterioration.

The age of the concrete in Figure 3 is unknown, but a similar cracking pattern was observed on a sidewalk known to be less than four years old.

This type of cracking in concrete differs from that attributed to frost action in two respects. First, the development of this type of cracking does not appear to initiate at edges or corners of slabs. Second, there appears to be little or no tendency for a dark surface deposit to form along these cracks, whereas such a deposit is frequently found along cracks associated with freeze-thaw action.

The authors' experience with this rock, plus the observation of an increased amount

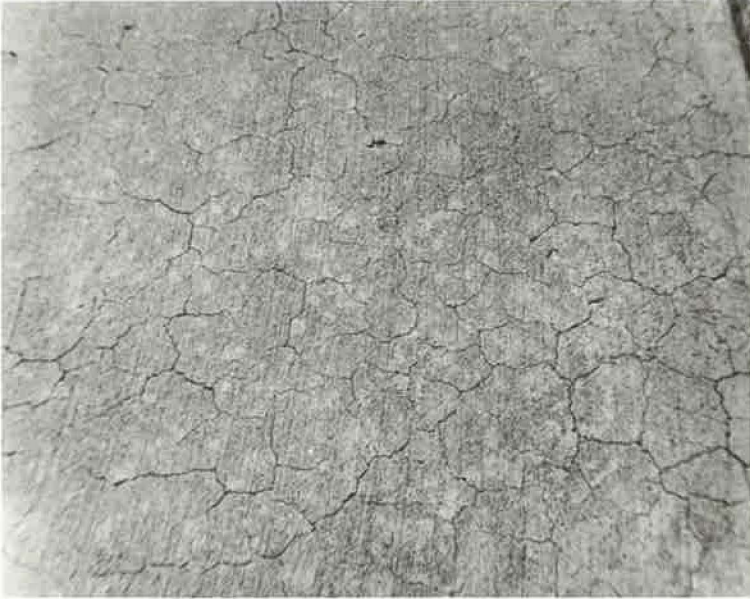


Figure 3. Cracking in concrete sidewalk.

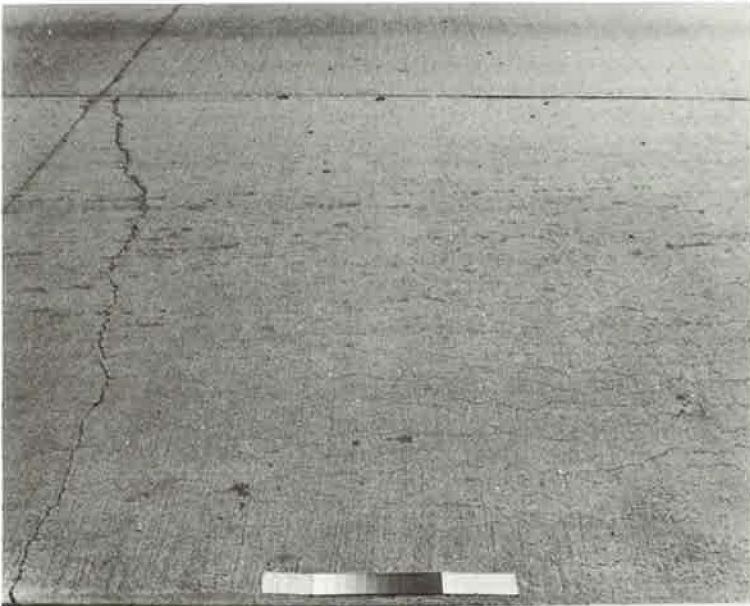


Figure 4. Cracking in PCC pavement.

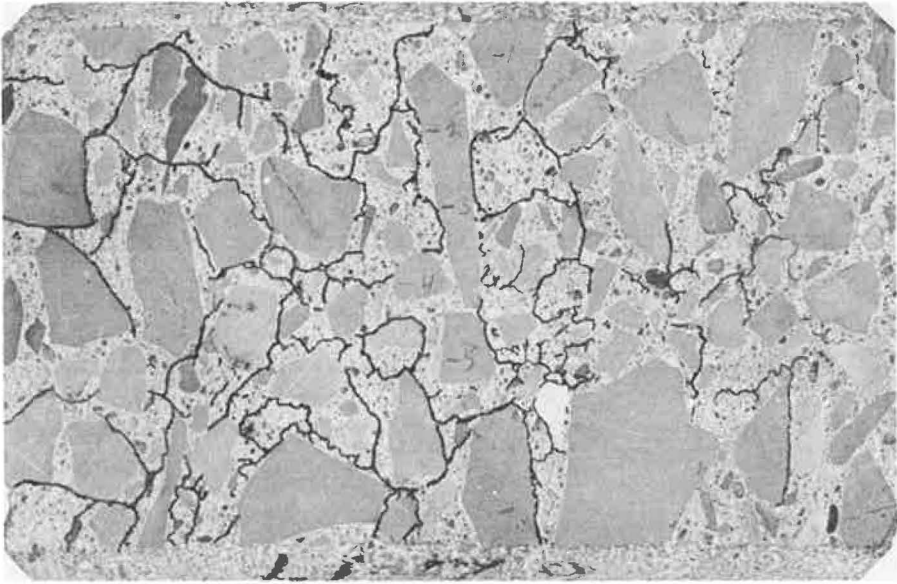


Figure 5. Microscopic cracking in PCC pavement.

of open pattern cracking (Fig. 4) on portland cement concrete pavements, created interest in the early published papers (1, 2, 3) on alkali-carbonate reactivity.

The extent of microscopic cracking in the interior of the concrete in Figure 4 is shown in Figure 5 (the cracks have been marked with ink). The interior cracking in this 8-yr-old pavement is rather extensive, and all of it would not be attributed to alkali-carbonate reaction. In some of the younger concretes microscopic cracks are few, short, and appear to originate at a coarse aggregate particle, suggesting that the cracking is a result of stresses induced by expansion of the aggregate. This association between cracking and coarse aggregate particles in Figure 5 is not too obvious. A possible reason for this is that, in this older concrete, other deteriorating factors, such as frost action, have probably been instrumental in developing the cracking into a network pattern.

Much of the cracking, which appears to be the result of a loss in bond between the coarse aggregates and the mortar (Fig. 5), is actually not loss in bond but is cracking in the mortar a short distance from and parallel to aggregate surfaces. At times this cracking occurs in the edge of a coarse aggregate particle and parallels the surface. In this sample very little of this latter type cracking in the aggregate particles was observed.

The only cracking in the aggregate particles which was inked, was that which extended into the cement paste. Such cracking in this sample was rare. The interior cracking in a few of the aggregate particles, which could not be traced into the surrounding paste, was not inked because such cracking appeared to be normal for crushed carbonate rock.

The extensive interior cracking in this concrete suggests that, at some future date, this pavement will develop deep-scale or serious structural failures. The probability of extensive disintegration of this pavement would be considered to be greatest in an area (as in Missouri) of numerous frost cycles.

Not only should this cracking of the concrete increase the probability of damage by frost action, but also the expansion resulting from deterioration should increase the possibility of blowups in the pavement. In addition, when the compression in the pavement is relieved by a blowup, the structural capacity of the cracked pavement should be greatly reduced.

There is presently little evidence of excessive expansion in the pavement shown in Figure 4, which has only contraction joints and exhibits more pronounced longitudinal than lateral cracks. This signifies that the pavement is in compression and is expanding laterally. However, this indication of lateral expansion has not been observed on all areas of pavement of this design which are affected by this type of cracking. In some areas the transverse cracks are more pronounced, which suggests that the main expansion has been longitudinal. There appears to be a possibility that some association might exist between the temperature of the concrete when placed, and the direction of primary cracking of the pavement. As concrete temperatures are not recorded in the construction records and relationship between temperatures of air and concrete is not constant, no attempt was made to determine if a relationship exists between air temperature at time of construction and the direction of predominant cracking.

Is the pattern cracking observed in Figure 4 caused by alkali-carbonate reaction? Tests (alkali-reactivity, described in next section) on small prisms, sawn from carbonate rock particles in the concrete, reveal that some of the rock particles are reactive. In addition, tests on small prisms, sawn from samples of ledge rock from the quarry which produced the aggregate, showed that the rock in one ledge was reactive. It is, therefore, concluded that the cracking in this pavement could well be due to alkali-carbonate reactivity.

As a result of the preceding, a rather extensive investigation of reactivity of Missouri carbonate rocks was initiated early in 1962. This investigation is one phase of a coarse aggregate study that has been approved by the Bureau of Public Roads and the Missouri State Highway Commission.

LABORATORY TESTS

To obtain an estimate of the number of possible sources of reactive carbonate rocks in Missouri, one sample of rock has been obtained from each ledge in numerous quarries in the state. This procedure does not provide an adequate sampling of the rock in each ledge, but it is expected that it will pinpoint the quarries or formations which should receive further investigation.

All rocks tested have not been approved for use in concrete, but almost all have either been approved or are being considered for such use.

From these small samples of rock, four small prisms (approximately $5/16 \times 5/16 \times 1.5$ in.) are sawn. Two each of these prisms are sawn perpendicular and parallel to the bedding plane.

These prisms are slightly larger in cross-section than those used by other investigators, but the increase in size tends to reduce breakage during preparation. It is also observed (Fig. 6) that the length comparator employed permits the use of square ends on the prisms. This innovation not only reduces the time required to prepare the prisms, but should also reduce errors in measurement due to the loss in material from the ends of a less blunt specimen.

The prisms were measured dry, immersed in distilled water until a constant length was obtained, and then each pair of prisms was placed in an airtight container with approximately 50 cc of 1N NaOH solution. At approximately weekly intervals (for 8 weeks) the prisms were removed from the containers, rinsed lightly by dipping in distilled water, surface dried, measured, and returned to the alkaline solution. In some instances measurements have been continued beyond the 8-week period.

In addition to the prism test, the chemical composition of all rocks exhibiting reactivity, and of many rocks exhibiting no reactivity, is being determined. The percent of dolomite in the carbonate fraction is calculated from the results of the chemical analysis.

Exploratory tests have been made on 2- x 2- x 11.25-in. concrete bars containing some of these coarse aggregates. Some of these tests are designed to determine the effect of (a) variations in the alkali content of the cement, and (b) exposure to calcium and sodium chloride solutions, on the expansion of the concretes made with reactive rock.

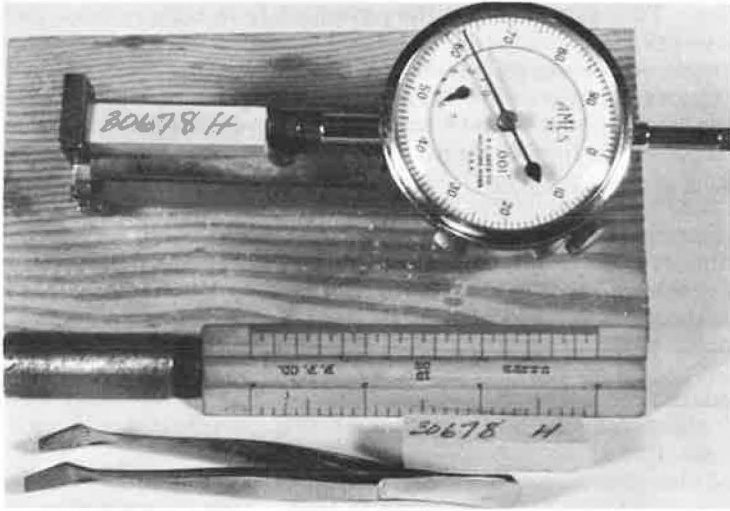


Figure 6. Comparator for measuring small rock prisms.

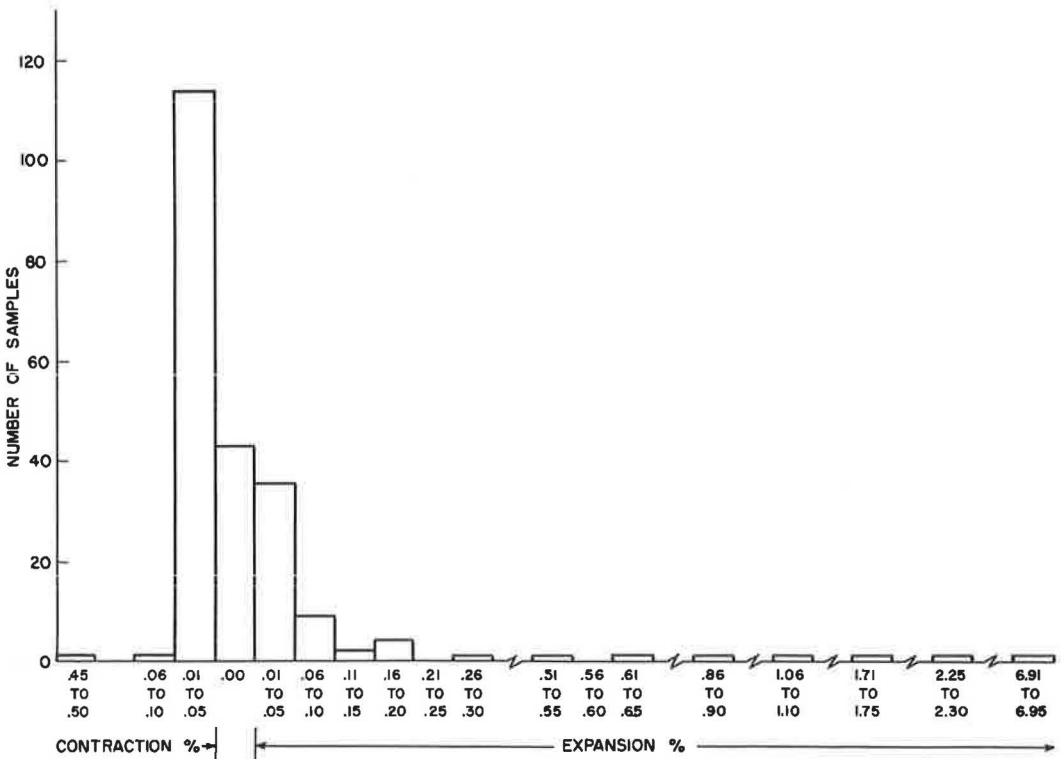


Figure 7. Distribution of prism expansions and contractions (average of two prisms perpendicular to bedding plane).

RESULTS OF TESTS

As of July 15, 1963, tests were completed on 218 sets of prisms sawn from rocks obtained from 23 geological formations, 47 quarries, and more than 200 ledges. Of these 218 sets of prisms, 23, or 10.5 percent, show definite indications of reactivity, or expansion of 0.06 percent or more in 8 weeks. All of the reactive stones were from six geological formations in the Ordovician, Devonian, and Mississippian systems.

The distribution of the prism expansions and contractions, for prisms perpendicular to bedding plane, is shown in Figure 7. It is noted that 116 (53 percent) of the prisms contracted during the test; 43 (20 percent) showed no change in length; 36 (16.5 percent) showed expansion of from 0.01 to 0.05 percent; 15 (7 percent) showed expansion of from 0.06 to 0.20 percent; and 8 (slightly less than 4 percent) showed expansion of from 0.21 to 6.95 percent.

In general, the expansion of the prisms taken perpendicular to the bedding plane was greater than that of prisms taken parallel to the bedding plane. There were, however, some exceptions to this general trend and there were two instances where the expansion parallel to the bedding plane exceeded 0.3 percent, while the expansion perpendicular to the bedding plane was less than 0.1 percent.

In addition, 14 prisms were sawn from 1- to 1.25-in. rock particles taken from the quarry tested in 1953, and used in the concrete beams previously discussed. To obtain prisms of maximum length, no attempt was made to saw them perpendicular or parallel to the bedding plane. At the end of 6 weeks, the expansion of these prisms varied from 0.00 to 5.82 percent with 7 of 14 showing expansion in excess of 0.20 percent, and with two additional samples showing expansion from 0.06 to 0.20 percent.

Figure 8 shows three samples of prisms exhibiting more than 4 percent expansion. The single prism is one of the 14 mentioned in the preceding paragraph, and the remaining four prisms are from two samples from the same ledge.

The chemical composition of 136 of the 218 samples was determined. The relationship between the percent dolomite in the carbonate fraction, the percent of acid insoluble, and the reactivity of these 136 carbonate rocks is given in Table 1.

Rock composition data for the 23 rocks showing 0.06 percent or greater expansion in 8 weeks are given in Table 2.

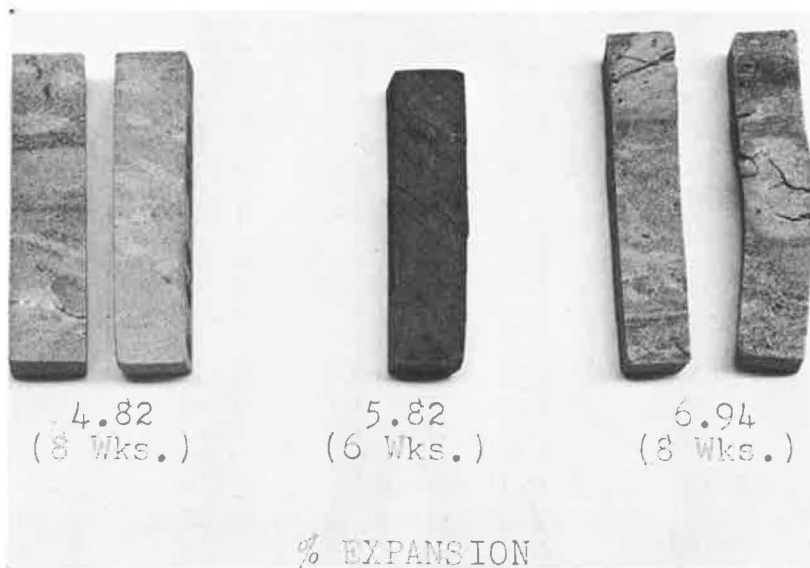


Figure 8. Three samples of prisms exhibiting high expansion.

TABLE 1
RELATIONSHIP BETWEEN PERCENT DOLOMITE IN
CARBONATE FRACTION, PERCENT ACID INSOLUBLE,
AND REACTIVITY OF CARBONATE ROCKS (136 Samples)

% Dolomite in Carbonate Fraction	No. of Samples	No. of Reactive ¹ Samples	% Acid Insoluble No. of Samples in Each Range ²				
			0 to 5	5 to 10	10 to 15	15 to 20	>20
0 to 10	79	4	67(1)	9(3)	3	0	0
10 to 20	9	6	4(3)	2(2)	2	1(1)	0
20 to 30	7	6	4(3)	2(2)	1(1)	0	0
30 to 40	8	1	7	1(1)	0	0	0
40 to 50	6	5	2(1)	4(4)	0	0	0
50 to 60	2	1	1	1(1)	0	0	0
60 to 70	0	0	0	0	0	0	0
70 to 80	0	0	0	0	0	0	0
80 to 90	0	0	0	0	0	0	0
90 to 100	25	0	7	10	6	0	2 ³
Totals	136	23	92(8)	29(13)	12(1)	1(1)	2(0)

¹Prisms showing 0.06 percent or greater expansion in 8 weeks.

²Number of reactive samples in each range enclosed in ().

³Not considered for use in portland cement concrete.

TABLE 2
ROCK COMPOSITION DATA FOR 23 ROCKS
SHOWING 0.06 PERCENT OR GREATER
EXPANSION IN 8 WEEKS

Sample	% Dolomite in Carbonate Fraction	% Acid Insoluble	% Expansion
8a	5.1	5.4	+0.194
8b	7.0	5.8	+0.070
13c	7.6	5.5	+0.181
8c	8.5	1.7	+0.140
15f	13.1	3.9	+0.082
8f	13.3	2.1	+0.074
8e	15.7	6.8	+0.524
12e	17.4	16.6	+0.07
8ll	19.7	6.8	+1.74
14p	20.0	4.7	+0.190
8oo	23.5	8.1	+0.155
12c	24.1	14.6	+0.88
8jj	24.8	3.1	+0.277
8r	27.1	2.8	+0.178
8dd	27.5	3.0	+0.080
12g	28.6	6.4	+2.304
8ccc	39.1	5.7	+0.073
8bb	40.6	6.3	+6.94
8d	43.1	5.5	+0.608
16i	44.8	3.0	+0.070
16f	46.9	5.1	+0.064
12h	47.9	5.4	+0.086
8hh	51.1	5.0	+1.073

In addition to these samples, the chemical composition of a sample of $\frac{1}{2}$ in. to No. 4 material from the quarry tested in 1953 showed the percent acid insoluble and the percent dolomite in the carbonate fraction to be 8.2 and 31.1, respectively.

Because tests on 2- x 2- x 11.25-in. concrete bars have been primarily exploratory and confined to a very few samples of rock, the results are not discussed herein. The tests do, however, show that the rate of reaction increases with increase in amount of alkali in the cement, and with exposure to a 4 percent solution of sodium chloride.

DISCUSSION OF RESULTS AND THE PROBLEM IN GENERAL

The preceding information and results show that some rocks in Missouri are reactive to alkali and of sufficient occurrence to cause concern. Furthermore, the results disclose that the chemical composition of reactive rock may differ appreciably from the previously suggested ranges (2) of 40 to 60 percent dolomite in the carbonate fraction, and 10 to 20 percent acid insoluble. This evidence seems to cast considerable doubt on the feasibility of eliminating reactive rock by a specification base on chemical composition.

Analysis of field surveys and laboratory test results suggest that the progressive type of pattern cracking (Figs. 3 and 4) is associated with alkali-aggregate reaction. However, in the early stages this cracking appears similar to a faint pattern cracking which, because of a negative indication of alkali-aggregate reaction, has been attributed to shrinkage of the concrete surface.

The question will undoubtedly be raised regarding acceptance or use of these reactive rocks in Missouri. So far as is known, none of the rocks exhibiting expansions in excess of 4.0 percent has been used in the concretes. As previously stated, the stone from one quarry was not approved because the concrete showed an excessive expansion. The other highly expansive stone came from a ledge which was not accepted for other reasons. For example, the rock in this latter ledge was recently rejected because of failure in the alcohol freeze test.

Present results, however, reveal that a reactive stone may meet all standard physical acceptance tests, including the alcohol freeze test. For example, a sample of the carbonate rock tested in 1953 was recently subjected to and passed the alcohol freeze test.

To date, no rock has been rejected because of expansion in the prism test. The time may come, however, when the results of this or some similar test will be sufficiently evaluated to permit their use in determining the acceptability of rock for use in portland cement concrete. Meanwhile the results of the prism test could be used to determine the need for more extensive testing of a rock in concrete prior to approval.

Blending of nonreactive and reactive stone has been suggested as a possible remedial measure in reducing expansions, caused by such chemical action, to an acceptable level. Perhaps, by chance, such a blend has been obtained with most reactive aggregates in the past. However, in some quarries, or benches therein, the nonreactive portion of the rock might be small or even nonexistent. This is believed to be the case at the quarry tested in 1953, although it cannot be verified as the quarry has since been abandoned and is presently flooded.

Dependence on a chance blend of reactive and non reactive rock is considered to be undesirable. In addition, a planned blending of reactive and nonreactive rocks appears to present problems. In the first place, it appears that the acceptable blend must be dependent on the degree of reactivity encountered. This means that, to insure an acceptable average reactivity for the total aggregate, the permissible amount of reactive rock should vary indirectly with the reactivity. In addition, good control might necessitate frequent testing of the rock in ledges showing variable reactivity.

Why does this problem appear to be more acute now than it has in the past? This problem refers to the type of cracking in concrete which appears to be associated with alkali-aggregate reaction. The present acuteness of the problem arises not from the fact that it has recently been associated with alkali-aggregate reaction, but because of its increased occurrence in relatively young concretes. Observed occurrences of such cracking in older concretes were so rare, or the rate of progression of the cracking

was so slow, that the cause of the cracking was considered to be of academic rather than of practical interest. In the newer concretes this type of cracking is not only increasing in frequency of occurrence but appears to be progressing at a faster rate.

The change in amount and rate of progression of this cracking might appear to be difficult to explain, especially in view of the fact that much of it is occurring in concretes containing aggregates from previously used sources. However, in analyzing the location of reactive ledges of rock in various quarries and the manner in which the quarries are being worked, it is obvious that the amount of reactive material being produced at any given time can vary from none to perhaps 100 percent. This possibility, plus the wide variation in the degree of reactivity being encountered, clearly discloses that the alkali-carbonate reaction that might occur in concrete could be highly variable. If the variability in the alkali content of the cement also is considered, it is apparent that fortuitous circumstances may have, until recently, either prevented extensive use of reactive rocks or their use with cements of high alkali content.

Although the preceding explanation is considered to be the most logical cause of the increased acuteness of this problem, some evidence has been obtained which indicates that the following factors may have, in some manner, contributed to either the amount or the rate of progression of the type of cracking under discussion. These factors are (a) increased amount of traffic (especially heavy loads), (b) increased use of air-entrained concrete, and (c) increased use of de-icing agents.

On dual highways this type of cracking tends to be worse in the traffic lane. This signifies that the increased amount of traffic on the newer highways may have contributed to the increased rate of progression of this type of cracking.

The results of tests on cores from one 5-yr-old pavement showed a tendency for the air content in the concrete in the more severely cracked areas to be near or greater than 6 percent, or above average for this project. This observed relationship between air content and rate of progression of this cracking does not appear illogical in view of the known reduction in concrete strength with entrainment of an excessive amount of air. This merely means that only insofar as the use of entrained air has contributed to a decrease in the strength of the concrete, it could have contributed to an increase in the rate of progression of this cracking.

Also, as previously mentioned, the results of exploratory laboratory tests show that the rate of alkali-carbonate reaction increased with exposure of concrete to a 4 percent solution of sodium chloride. Although these results are meager, the indication obtained appears to be verified by results of tests by P. Smith (5). In addition, extensive use of de-icers, resulting in ice- and snow-free pavements, should subject concretes to more frequent and more severe freezing which should tend to increase the rate of progression of this cracking.

Regarding fortuitous circumstances, a very recent discovery merits mention. In examining some cores drilled from a 5-yr-old pavement (previously mentioned in discussing the indicated effect of air content) exhibiting the type of cracking under discussion, considerable evidence of alkali-silica reaction was found. This evidence indicates that the siliceous fine aggregate and the chert in the coarse aggregate may both be involved. This therefore raises the probability that, at times, both alkali-silica and alkali-carbonate reactions may be occurring concurrently. So fortuitous circumstances may have prevented the use of a combination of materials that could have resulted in extensive and rapid deterioration of the concrete.

Does this type of cracking seriously affect the service life of a concrete pavement or structure? A study of the literature (1, 2, 3, 4, 5, and numerous others) tends to leave one in doubt as to the seriousness of this cracking. The impression is obtained that cracking beyond a certain degree is unacceptable, whereas less severe cracking is not expected to affect seriously the service life of the concrete. The problem is, how much cracking is acceptable? The answer to this question appears to be unknown, but undoubtedly all will agree that this type of cracking, however minor, cannot be other than detrimental to the resistance of concrete to frost action.

It is not believed that these two types of alkali-aggregate reaction have, independently or concurrently, been responsible for serious concrete deterioration in the older concretes used on Missouri highways; yet the information previously submitted suggests

that serious deterioration may develop in some of the younger concretes as a result of the combined deteriorating effect of alkali-aggregate reaction and other factors. This signifies that alkali-aggregate reactions need not be sufficiently severe to cause complete deterioration of concrete by themselves to be classified as practical problems. Factors, both physical and chemical, which cause deterioration of concrete tend to work concurrently, and not independently. Consequently, any factor contributing to concrete deterioration cannot be ignored. For example, a slight amount of alkali-carbonate or alkali-silica reaction may, with certain materials, greatly increase the rate of deterioration of concrete by frost action.

To prevent concrete deterioration from exceeding the small percentage of acceptability, it is believed necessary to consider as practical problems, all factors contributing to concrete deterioration.

SUMMARY

Because this is a progress report, the following should be considered as indications rather than conclusions:

The observed increased amount of a progressive type of pattern cracking in younger concretes, the apparent association of alkali-aggregate reaction with this type of cracking, and the demonstrated reaction between several carbonate rocks and alkali, all tend to verify that alkali-carbonate reactivity is now a practical problem in Missouri.

The results obtained also disclose that the chemical composition of reactive rock may differ appreciably from the previously suggested ranges of 40 to 60 percent dolomite in the carbonate fraction, and 10 to 20 percent acid insoluble.

Suggested primary causes of the increased cracking in concretes attributed to alkali-aggregate reactions are chance use of (a) a higher percentage of reactive aggregate, or (b) aggregate of higher reactivity, or (c) combinations of materials which increase the amount and rate of reaction.

Suggested secondary factors, that appear to have contributed to an increase in either the amount or the rate of progression of this cracking are increased (a) amount of traffic, (b) use of air-entrained concrete (only insofar as it may contribute to a decrease in the strength of the concrete), and (c) use of de-icing agents (insofar as some may contribute to the reaction and all may contribute to an increase in the number and severity of freezing-and-thawing cycles).

As reactive rocks can and often do pass all present acceptance tests, there is a definite need for recommendations concerning the acceptance or use of reactive rocks. Although such recommendations are not included, it is suggested that any blend of reactive and nonreactive rock should be such as to insure an acceptable service performance.

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