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Foreword

Although the study of reactive carbonate aggregates is a relatively new development in concrete research, the rapidity with which data have been developed and the scope of the research to date are impressive. The Committee on Performance of Concrete—Chemical Aspects early recognized the importance of this area of research and asked a subcommittee to arrange a symposium on the subject. It was the opinion of the Committee that such a discussion of the subject at an early stage would be of great benefit in coordinating the various research efforts.

Although no attempt is made to summarize the conclusions of the various papers, it seems desirable, particularly in view of the relatively recent recognition of the problem, to make several observations and to suggest several cautions to the reader.

First, the papers seem to suggest that just as the term "alkali-aggregate reaction" subsequently was broadened to include several types, the term "alkali-carbonate rock reaction" must be used with prudence because several manifestations and mechanisms are involved which may or may not be related. Reaction can not be used synonymously with expansion, because there is evidence that some reactions do not result in expansion. Thus separation of the relatively straightforward behavior of the expansive alkali-carbonate rock reaction in concrete from cases in which performance is complicated by other physical or chemical properties of the aggregates is necessary. This separation may be made by relatively simple expansion measurements on concrete or on rock prisms, using rock which is otherwise satisfactory as concrete aggregate.

The over-all performance of concrete is often complicated by a number of interactions, making it difficult to single out any one factor as the cause of an observed phenomenon. The discovery of alkali-silica reaction provided a convenient answer to many perplexing questions, some of which subsequently proved to relate to other phenomena. Likewise, there are many current questions to which the alkali-carbonate reactions would offer a convenient, but incorrect, answer.

Even though reactive carbonate rock is widely distributed geographically, and is locally abundant in isolated areas, it must be borne in mind that most of the very large volume of carbonate aggregates used have provided and will continue to provide excellent service in concrete. Thus, in applying the findings of research, such as those reported here, to specifications and construction situations, specifications writers, purchasers, and consumers, must be certain that their action is directed toward the proper problem, is tempered with appropriate engineering judgment, and does not ignore existing service records. Likewise, producers of aggregates must recognize the ultimate consequences of ignoring the reaction and become better informed on the behavior of their products in a variety of uses.

A careful study of the papers and discussions included here will show that there are some apparent discrepancies in the results reported by the various authors. This is to be expected from initial studies such as those reported, which involve various new techniques and different laboratory conditions. A major contribution of the Symposium will be to focus attention on these areas of uncertainty so that future workers may refine and extend the knowledge of the reactions. The papers also emphasize the need for standardization of testing procedures. However, as the papers are studied, one is impressed with the general agreement of the authors on major fundamental points.

Finally, the papers in this Symposium present a considerable volume of data on the chemistry of the reactions, the behavior of reactive aggregates in concrete, and the geographical distribution and geological characteristics of reactive rocks. Sufficient field studies have been presented to indicate the need for some control of certain carbonate aggregates. The task of determining through systematic study the extent and nature of such controls remains. The great need at this point appears to be systematic and documented studies to correlate the various laboratory results with service records and field performance.

It should be apparent to the reader that a volume of the magnitude of this one is the result of the concentrated efforts of many individuals. As Chairman, I would like to acknowledge and express the appreciation of the Committee for the excellent cooperation received from the authors and from the committee members who accomplished in detail and with dispatch the 42 reviews involved. Special thanks are also extended to W. J. Halstead, former Chairman of this committee, and to W. C. Hansen, Chairman of the Symposium Subcommittee, for their leadership in their respective capacities.

Howard Newlon, Jr., Chairman
Committee on Performance of
Concrete—Chemical Aspects

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Part I. THEORETICAL STUDIES

Alkali Reactivity of Dolomitic Carbonate Rocks

DAVID W. HADLEY, Research Geologist, Applied Research Section, Portland Cement Association

The performance of the alkali-reactive carbonate rocks in field and laboratory concretes is described, and previously published and unpublished research concerning the causes and mechanisms of reactivity is reviewed and discussed. Known occurrences of potentially reactive rocks are noted, rapid laboratory tests for the recognition of the reactive rocks are summarized, and various remedial measures are discussed.

•THIS PAPER was written at the request of HRB Committee on Performance of Concrete—Chemical Aspects to provide for this symposium a paper setting forth the current "state of the art" regarding the alkali reactivity of carbonate rocks. The compilation of the current knowledge concerning the rocks of this type has necessitated the inclusion of previously unpublished work. In addition, on the basis of both the existing literature and his own research, the author has attempted to synthesize a series of working hypotheses which would seem, on the basis of current knowledge, to best explain the observed behavior of the reactive rocks. For the reader who desires a more detailed review of the literature, the writer has also prepared a comprehensive annotated bibliography which is published as a part of this symposium.

The great majority of dolomitic rocks is for practical purposes chemically inert in alkaline environments and, if physically suitable, makes excellent concrete aggregates. Certain fine-grained and argillaceous dolomitic rocks have been found, however, to be chemically reactive in concrete. For convenience, these reactive rocks can be divided into two main types: (a) those which expand in alkaline environments, and (b) those which develop prominent siliceous reaction rims in concrete.

Each of these reactive rock types is discussed separately. The performance of each type in field and laboratory concretes is described, known occurrences of potentially reactive rocks are listed, and various remedial measures are discussed. In addition, previously published and unpublished studies concerning the causes and mechanisms of reactivity are reviewed and discussed, and tests for the recognition of the reactive rocks are summarized.

The relationship as presently understood between the two types of reactive rocks is shown, and the factors believed to determine the type of reactivity which a rock would exhibit in concrete are briefly outlined.

Paper sponsored by Committee on Performance of Concrete—Chemical Aspects.

EXPANDING ROCKS

Nature of Problem

Concrete distress attributable to expansive carbonate rocks was first described by Swenson (1) who studied concrete structures in the vicinity of Kingston, Ontario.

The basic symptom of the reaction was a rapid expansion of the concrete with attendant cracking. Where a differential in moisture content existed between the top and bottom of the affected concrete, as in sidewalks and curbs, a very characteristic pattern of map cracking was produced, sometimes as soon as two or three months after placing. The distance between cracks was about 2 to 4 in. and in sidewalks the cracks were found to extend about two-thirds of the depth of the slab. In a subsequent paper, Swenson and Legget (2) estimated that 75 percent of the concrete in the Kingston area had been affected by the carbonate-aggregate reaction (Fig. 1).

Laboratory studies, conducted by Swenson (1) and Swenson and Gillott (3) showed that the poor performance of certain of the Kingston concretes could be correlated with the use of coarse aggregate from specific beds of local quarries. Although concrete prisms made with rocks from these beds showed the characteristic expansion and cracking, the aggregate itself was not shown to be potentially alkali reactive by the mortar bar test (ASTM C 227-52T), the Quick Chemical test (ASTM C 289-54T) or the Conrow test (ASTM C 342-55T), and some as yet unrecognized form of chemical reactivity was suspected.

In separate but concurrent research, Swenson and Gillott (3) and Hadley (4) found that when samples of the reactive Kingston aggregate were placed in highly alkaline solutions, a very rapid expansion of the rock took place.

Factors Influencing Concrete Expansion.—The work of Swenson (1) and subsequent detailed studies by Hadley (7) and others show that the following factors significantly influence the rate of expansion of concretes made with the reactive aggregates.

1. Cement alkali content. The rate of expansion of the concrete is a direct function of the alkali content of the cement (Fig. 2).

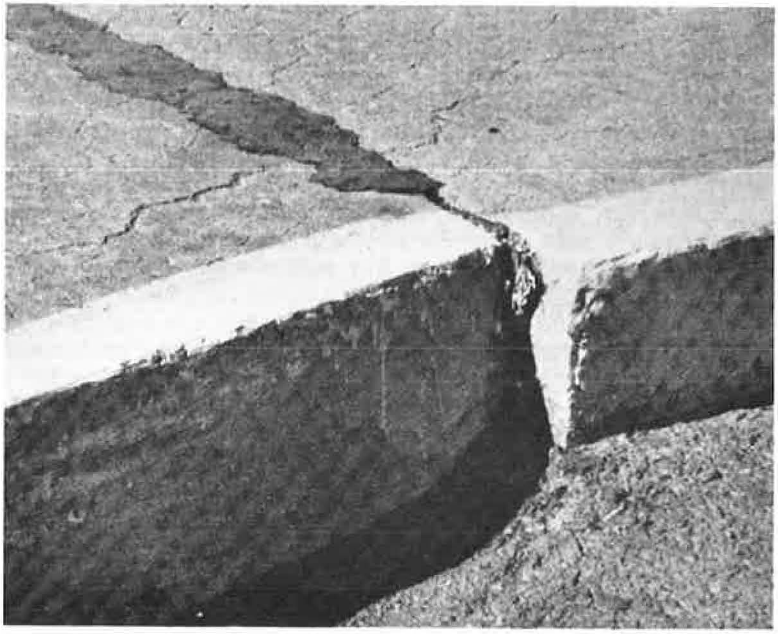


Figure 1. Map cracking and expansion of concrete in Kingston, Ontario, reflects the expansion of the alkali-reactive aggregate particles (2).

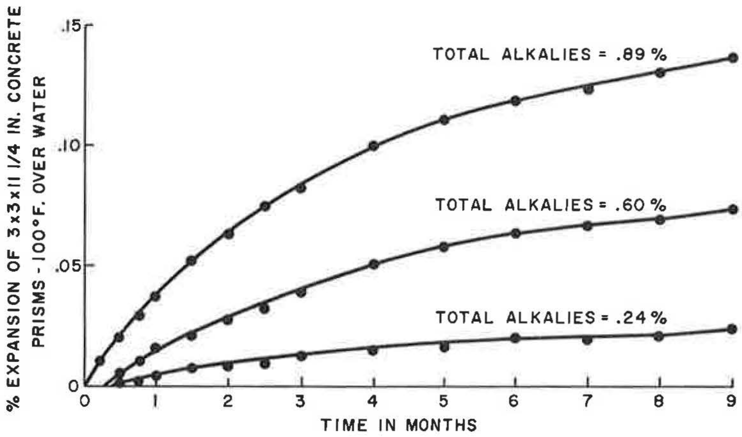


Figure 2. Rate of expansion of concrete is influenced by alkali content (Na_2O equivalent) of cement (7).

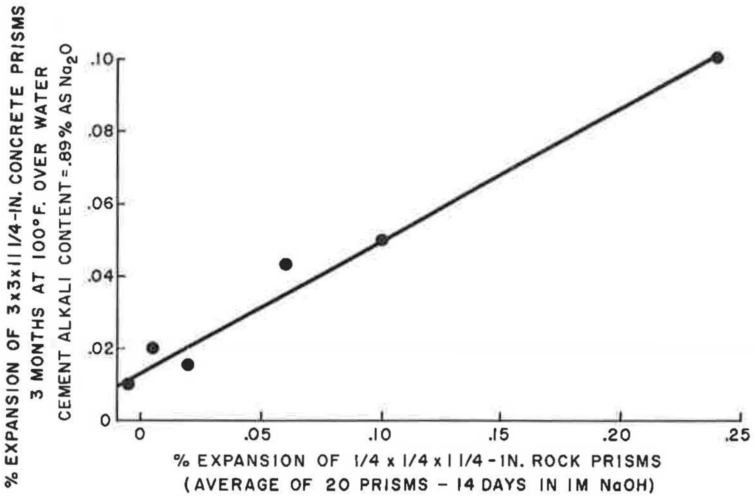


Figure 3. Expansion of small rock prisms in alkaline solution correlates well with expansion of concretes made using these rocks as aggregate (7).

2. Expansive reactivity of rock. The correlation between the rate of expansion of the reactive rocks in alkali and the expansion of concretes made with these rocks is good (Fig. 3).

3. Temperature and moisture conditions. Expansion of the affected concrete is greatly accelerated by warm, moist conditions.

4. Maximum aggregate size. Swenson (1) found the amount of concrete expansion decreased with decreasing maximum aggregate size (Fig. 4).

Nature of Expansive Rocks

All of the expansive rocks which have been studied to date have been found to be (a) dolomitic, (b) argillaceous, and (c) extremely fine grained. Most of the highly reactive rocks are argillaceous dolomitic limestones, containing mixtures of calcite and dolomite and appreciable amounts of clay-sized acid-insoluble residue. In addi-

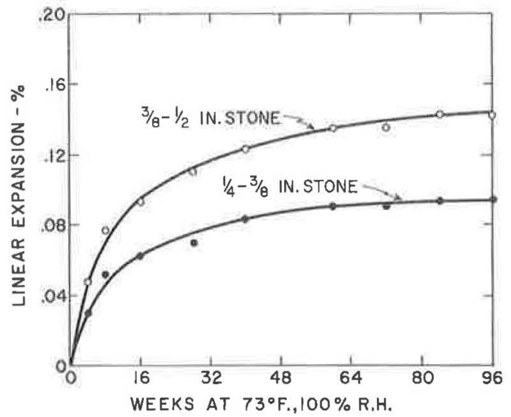


Figure 4. Effect of maximum size of reactive limestone on expansion of concrete (3).

tion, all of these highly reactive rocks display a characteristic texture, consisting of small isolated dolomite rhombs "floating" in a matrix of clay and finely disseminated calcite.

Distribution and Abundance of Expanding Rocks. — Expansive rocks have been identified from Ontario, Virginia, New York, Indiana, Illinois, Wisconsin, Iowa, Missouri, and South Dakota. Comprehensive field surveys in Indiana by Hadley (7) and in Virginia by Newlon and Sherwood (5) show that in both of these areas the reactive rocks are fairly common throughout the exposed sequences of carbonate rocks. It would appear likely that potentially reactive rocks are present in most of the geographic areas in which carbonate rocks are exposed.

Physical Characteristics of Expansive Rocks.—A number of the expansive rocks from the eastern United States and Canada are of sufficiently good physical quality to pass the existing acceptance tests such as specified in ASTM C 33 or AASHO M 80 and have in some cases been used, with unfortunate consequences, as concrete aggregate. Although isolated examples of physically sound but alkali-expansive rocks are also found in the midwestern states, the reactive rocks from this region are usually of much poorer quality and consequently have not been as widely used as aggregate.

Mechanisms of Reactivity

Dedolomitization Reaction.—X-ray diffraction studies of expansive rocks which have been reacted with solutions of the alkali metal hydroxides show a decrease in the amount of dolomite present, an increase in calcite content, and the appearance of brucite. Further laboratory studies by Hadley (4) have shown that this change in mineral composition is the result of a chemical reaction between the dolomite in the reactive rocks and solutions of the alkali metal hydroxides.

This reaction can be written as

$$\underset{\text{dolomite}}{\mathrm{Ca\,Mg(CO_3)_2}} + 2\,\mathrm{M\,OH} \rightarrow \underset{\text{brucite}}{\mathrm{Mg(OH)_2}} + \underset{\text{calcite}}{\mathrm{CaCO_3}} + \mathrm{M_2CO_3}$$

in which M represents K, Na, or Li.

In concrete, the alkali carbonate produced by this reaction will react with hydration products of portland cement; for example,

$$\mathrm{Na_2\,CO_3} + \mathrm{Ca(OH)_2} \rightarrow 2\mathrm{NaOH} + \mathrm{CaCO_3}$$

This type of reaction regenerates the alkalies and thereby permits continued reaction with the dolomite.

Factors Influencing Reaction Rate of Dolomite.—In order to study the dedolomitization reaction in greater detail, a series of experiments (4) was performed by the author using prepared mixtures of reagent-grade calcium carbonate and a well-crystallized dolomite. The amount of dolomite reacted was estimated from a chemical determination of the amount of soluble carbonate ion released during immersion in alkali hydroxide solutions. The previously unpublished details of the methods used are given in Appendix A. In these experiments it was found that the rate of reaction of dolomite in alkaline solutions depends on the following:

1. Dolomite grain size. As would be expected, the rate of reaction increases with decreasing grain size—i.e., increasing reactive surface.

2. Amount and grain size of associated calcite. The rate of reaction of dolomite is greatly increased by the presence of calcite. The degree of acceleration is a direct function of both the amount and grain size of the admixed calcite (Fig. 5).

While the percentage of dolomite reacted in calcite-dolomite mixtures is greatest for the mixtures highest in calcite, the relationship between rate of reaction and the amount of dolomite available for reaction is such that the greatest amount of dolomite is reacted in mixtures containing approximately equal amounts of calcite and dolomite (Fig. 6).

3. Solution strength. The effect of variations in solution strength on the rate of dolomite reaction also is affected by the amount of associated calcite.

a. Dolomite—In the absence of calcite, the rate of reaction is independent of hydroxide concentration over the range 0.5M to 1M NaOH (Table 1).

b. Calcite-dolomite mixtures—As is also shown in Table 1, the rate of reaction of dolomite in calcite-dolomite mixtures tends to increase with increasing alkali concentration and increasing calcite-dolomite ratio.

4. Ionic species. It was found by Hadley (4) that the order of reactivity of the alkali metal hydroxides in solutions of equal acitivity was

Na > K > Li

Mechanisms for Expansion.—Three hypotheses have been advanced to explain the expansion of the reacting aggregate particles.

1. Expansion of dolomite crystals. Measurements made by Hadley (4) on a single crystal of dolomite during the dedolomitization process disclosed an expansion of 0.15 percent at 100 days. It would therefore seem likely that at least a part of the expansion of the reactive rocks may be due to the expansion of the individual dolomite crystals in the rock.

2. Hypothesis of Feldman and Sereda. Feldman and Sereda (6) studied the sorption and expansion isotherms of reactive Kingston, Ontario aggregate before and after treatment with alkaline solutions and postulated the presence of trace amounts of colloidal material within the pores of the reacted rock. This material was considered to be produced either by or in association with the dedolomitization re-

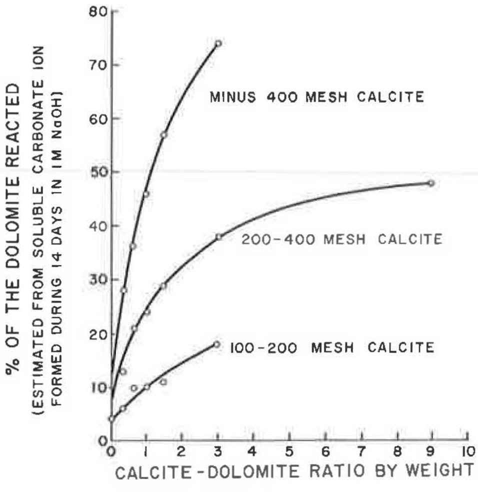


Figure 5. Rate of reaction of 200-400 mesh dolomite in laboratory mixtures is a function of amount and grain size of admixed calcite.

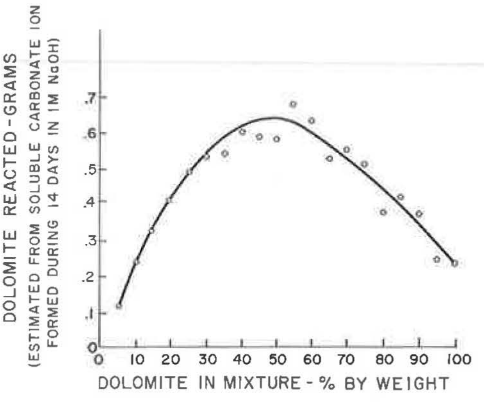


Figure 6. The greatest amount of dolomite was reacted in mixtures containing approximately equal amounts of calcite and dolomite.

TABLE 1

REACTION OF DOLOMITE IS ACCELERATED BY ALKALI AND IS ALSO A FUNCTION OF CALCITE-DOLOMITE RATIO

Sodium Hydroxide Concentration	% of Dolomite Fraction Reacted[1]		
	Calcite-Dolomite Ratio		
	0.5	1.0	1.5
1.0 molar	51.0	65.2	70.7
0.75 molar	53.0	63.5	70.0
0.50 molar	50.0	62.0	67.8
0.25 molar	45.0	49.3	49.0
0.10 molar	25.0	44.3	44.3
0.05 molar	29.5	29.5	29.5

[1] Various mixtures of calcite (2, 4 or 6 grams) and dolomite (4 grams) were immersed for 14 days in alkali solutions containing 1.8 grams total NaOH diluted to the indicated concentrations.

action, and the expansion of the rocks was attributed to the swelling of these colloidal materials in the presence of water.

3. Osmotic hypothesis. Studies which are described in Appendix B, would suggest that the observed expansion could be due, at least in part, to pressures built up at the individual dolomite crystals by the differences in flow tendencies, through the interstitial clay, of the alkali-carbonate solution produced in the dedolomitization reaction and the pore solutions containing the alkali hydroxides.

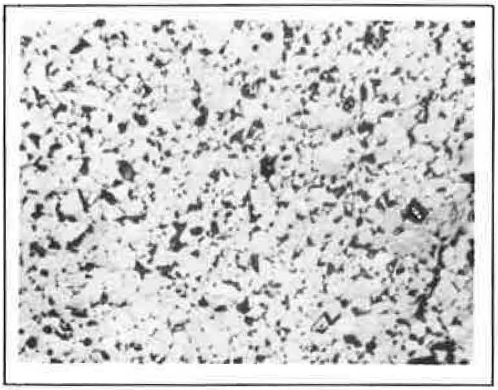
Role of Clay in Expansion of Reactive Rocks.—One of the outstanding characteristics of the reactive rocks is their high clay content. (Clay is used here as including all non-carbonate material in the rock having an equivalent spherical diameter of two microns or less. Clay contents were normally determined by subtracting from the total acid-insoluble residue the percentage of silt-sized and larger particles as estimated by petrographic techniques.) Research, which is described later in this paper, has shown that there is apparently a critical clay content below which rocks of any given carbonate composition will not significantly expand in alkali, and as a general rule, the expansion shown by reactive rocks of a given carbonate composition increases as the clay content increases. It has been found however, that the type of clay mineral making up the bulk of the clay-size fraction has no appreciable effect and that the presence of clay has no accelerating effect on the rate of reaction of dolomite in alkaline solutions.

The clay component of the expanding carbonate rocks is thought to influence the expansion of these rocks in two ways.

1. Interstitial clay as an osmotic membrane. The strong possibility that clay membranes play an important role in the expansive mechanism was previously described.

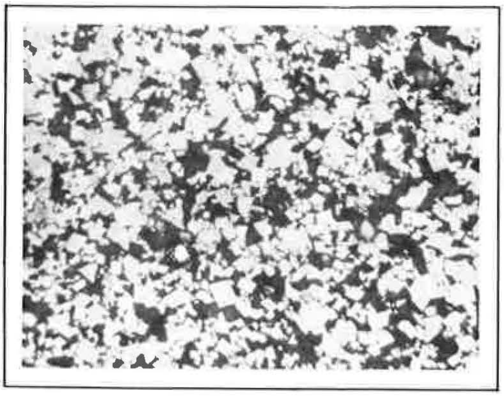
2. Structural weakening through dilution with clay. Figures 7 through 9 are a series of photomicrographs of argillaceous dolomites containing progressively larger amounts of clay and showing progressively greater expansive tendencies. In Figure 7 it can be seen that in a rock of low clay content the dolomite rhombs are largely interpenetrating and form a rigid structural framework. In Figure 8 the rock contains a much higher percentage of clay, the structural framework of the rock has been disrupted, and many of the dolomite rhombs are no longer tied to their neighbors through interpenetration. In Figure 9 the process of dilution with clay is carried a step further and the rock consists largely of isolated dolomite rhombohedra "floating" in a clay matrix.

As the percentage of clay in the rock increases, there is a progressive disruption of the internal carbonate skeleton. As shown by the relative expansions of the rocks



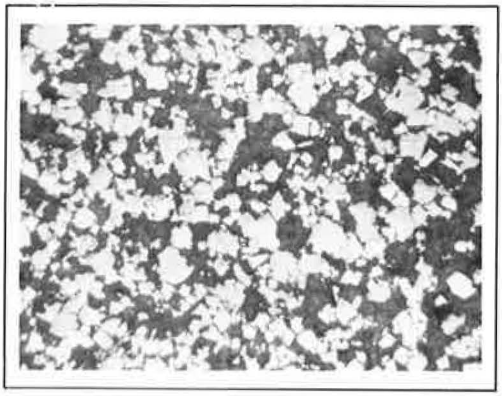
APPROXIMATELY 7 % CLAY
EXPANSION IN ALKALI = .07 %

Figure 7. In rocks with low clay contents interpenetrating dolomite crystals form rigid structural framework and expansion is low.



APPROXIMATELY 15 % CLAY
EXPANSION IN ALKALI = .74 %

Figure 8. As clay content increases, carbonate skeleton is disrupted and weakened and significant expansion may occur.



APPROXIMATELY 25 % CLAY
EXPANSION IN ALKALI = 1.20 %

Figure 9. Large expansions occur when carbonate skeleton is sufficiently weakened through dilution with clay no longer restraining expansive forces produced by dedolomitization reaction.

depicted in Figures 7 through 9, this causes a decrease in the ability of the rock to withstand the expansive forces produced by the reaction of the dolomite and an attendant increase in expansion.

Relationship Between Texture and Reactivity.—Highly expansive rocks all share a very characteristic texture. If the basic elements of this texture are examined in the light of what is known about the various factors influencing reactivity, the role of texture in the reactivity of these rocks becomes more understandable.

The rocks were described as consisting of small isolated dolomite rhombs "floating" in a matrix of clay and finely disseminated calcite. The basic elements of the texture therefore would be:

1. Very fine-grained dolomite. Because the rate of reaction of dolomite increases with decreasing grain size, the dolomite in the expansive rocks is present in its most reactive form.

2. Associated calcite; also extremely fine grained. The presence of associated calcite has been found to accelerate greatly the dedolomitization reaction, and as shown in Figure 5, the rate of acceleration increases with decreasing calcite grain size.

3. Abundant interstitial clay. Clay is thought to affect expansion through osmotic effects and through a dilution and weakening of the carbonate skeleton of the rock which

lessens the ability of the rock to withstand the expansive forces generated by the dedolomitization reaction.

Tests for Recognition of Expansive Carbonate Rocks

Utilizing what is known about the influence exerted by the texture and composition of the expansive rocks and their behavior in alkaline solutions and in concrete, the following tests for reactivity have been developed.

1. Petrographic examination. Although it is not yet possible to identify the expansive rocks positively by petrographic techniques, it is possible to differentiate rapidly between potentially reactive and obviously non-reactive rocks. For this reason, petrographic examination provides a valuable screening technique which can reduce effectively the number of tests necessary in any investigation.

The following characteristics of the reactive rocks are readily determined by petrographic techniques:

a. Grain size—All of the reactive rocks are characterized by an extremely fine grain size (about 50 microns or smaller).

b. Composition and texture—All of the reactive rocks are dolomitic, and the dolomite is in every case largely present in the form of small euhedral crystals.

Most of the highly reactive rocks also contain appreciable amounts of calcite. The mode of occurrence of the calcite is very important. It has been found that areas of sparry calcite cement or large calcitic fossil fragments have no appreciable effect on reactivity and that it is only when the calcite is finely disseminated throughout the matrix that increased reactivity results.

The degree to which the carbonate skeleton has been disrupted through clay dilution is also apparent under the microscope.

2. Test for expansion in alkali. A rapid determination of reactivity can be made by immersing small rock prisms in alkaline solutions and periodically measuring the prisms for expansion. Results of these tests have been found to correlate well with data from concrete and mortar bar tests. A full description of this test method is given by Hadley (4).

3. Mortar bar tests. In studies of the expansive rocks from Indiana, Hadley (7) found that the more reactive rocks failed the standard mortar bar test (ASTM C 227-61T) when used in conjunction with a cement containing 0.89 percent total alkalies. Swenson (1) found, however, that mortar bars made with reactive Kingston limestone did not show a deleterious amount of expansion. The reason for this difference in behavior is not known and research is now under way to elucidate this point.

4. Concrete tests. As developed by Swenson, the basic test for expansive reactivity of carbonate rocks is to measure the expansion of concretes made with the rocks in combination with cements of high alkali content. Significant expansion takes place within the first month, and the rate of expansion can be increased by storing the test specimens at elevated temperatures in sealed containers over water.

Possible Remedial Measures.—Although pozzolanic replacements or additions of lithium salts, both of which are effective in modifying the alkali-silica reaction, have been found by Swenson (1) to have no significantly beneficial effect in concretes made with the expansive carbonate rocks, several measures can be taken to minimize the amount of concrete expansion.

1. Dilution with non-expansive aggregate. Unlike the alkali-silica reaction, in which there is a "pessimum" amount of reactive material, relationships in the alkali-carbonate reaction are straightforward. Expansion is decreased by an amount roughly proportional to the extent of dilution with inert material. In many occurrences the reactive rocks constitute only a small percentage of the carbonate rocks exposed, and control would simply be a matter of insuring that adequate mixing and attendant dilution occurred during the quarrying and screening operations. As a case in point, certain zones of the Ste. Genevieve formation in Indiana were found by Hadley (7) to contain beds of moderately to highly reactive rock. In every case, however, these reactive beds constitute only a small percentage of the face being quarried and the Ste. Genevieve has earned a reputation as being one of the finest sources of concrete aggregate exposed in the state.

2. Limitation of maximum particle size. Although in most cases this measure would not in itself be sufficient to allow the safe utilization of the reactive aggregates, it would provide added protection when used in cooperation with other methods.

3. Use of low alkali cement. This method might be effective with moderately reactive materials, but the data presented in Figure 2 show that appreciable expansion might take place even with cements of low alkali content. It would therefore appear advisable to couple the specification of cement-alkali content with dilution with inert aggregate and limitation of top aggregate size if at all possible.

RIM-DEVELOPING ROCKS

Nature of Problem

In 1958, Bisque and Lemish (8) and Lemish, Rush, and Hiltrop (9) described distressed concrete pavements in Iowa. These pavements were characterized by a progressive cracking and spalling at joints and edges of the pavement and a general weakening of the concrete. Distress had become evident after 5 to 15 years of service. Figure 10 shows an affected Iowa pavement. Petrographic examination of certain of the affected concrete showed that in some cases the carbonate coarse aggregate particles had developed prominent reaction rims and that the interstitial cement paste appeared to be highly carbonated. Figure 11 shows typical reaction rims in concrete.

The reaction rims, studied in detail, were found to be less porous and to contain more silica than the interior of the aggregate particles. When the affected concrete was etched with dilute acids, the silicified rims were appreciably less soluble than either the interior of the rock or the surrounding cement paste.

The development of these silicified reaction rims was considered evidence of a type of deleterious cement-aggregate reaction involving silica but different from the ordinary alkali-aggregate reaction.

Subsequent investigations have shown that very similar concrete distress has occurred in many pavements containing carbonate aggregates which do not develop reaction rims and it is not presently known whether the development of rims per se, is indicative of a deleterious chemical reaction.

Rim-Developing Rocks in Concrete.—Bisque and Lemish (10) found that certain rim-developing rocks from Iowa had a detrimental effect on the rate of strength development of concrete. In similar experiments at the Portland Cement Association laboratories (Table 2), it was found that in concretes made with a rim-developing rock

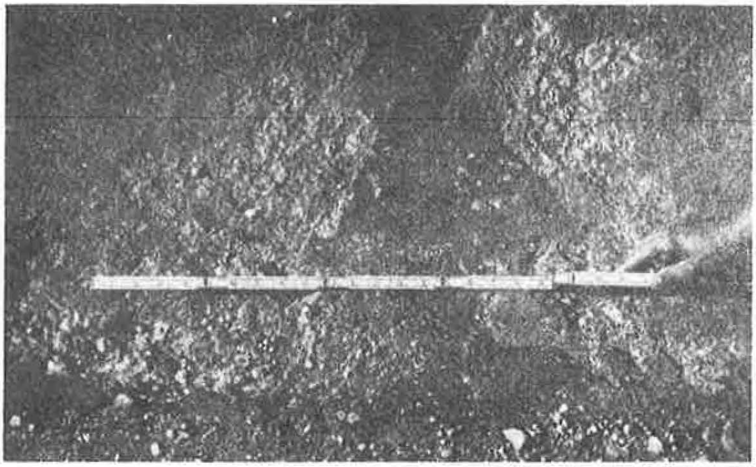


Figure 10. Deterioration of this Iowa pavement attributed to rim-developing carbonate coarse aggregate (14).

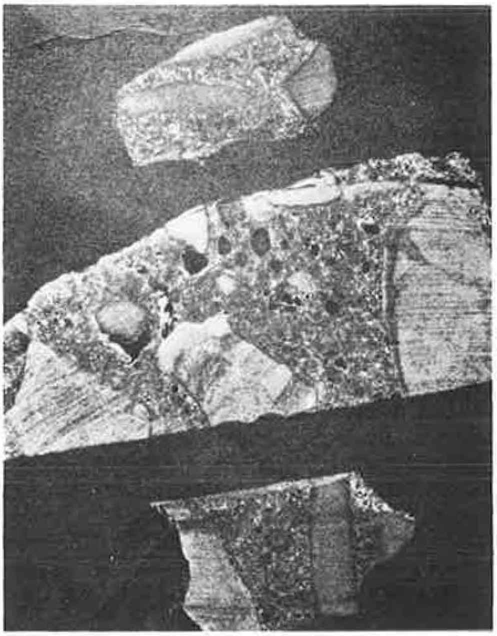


Figure 11. Typical reaction rims in concrete (14).

from Indiana there was actually a slight decrease in strength with time under certain storage conditions. It should be noted, however, that the 1-yr compressive strengths ranged between 6,000 and 9,000 psi, depending on storage conditions, and certainly remain at an adequate level. Research is being continued to determine whether there is any long-term strength loss, and whether this loss would be sufficient to cause detrimental effects in field concrete.

Distribution and Abundance of Rim-Developing Rocks.—Rim-developing rocks have been identified from Ontario, Indiana, Illinois, Minnesota, Iowa, Missouri, and Wisconsin. These rocks are similar in nature and mode of occurrence to the expansive carbonate rocks. It is likely that rocks susceptible to rim development in concrete are present in all major areas of carbonate rock outcrop.

Physical Characteristics of Rim-Developing Rocks.—The rim-developing rocks are similar to the expansive rocks in composition and texture. The major difference between the two groups is in their clay content; the rim-developing rocks contain appreciably less clay than the equivalent expansive rocks. The rim-

TABLE 2

RIM-DEVELOPING ROCKS INFLUENCE RATE OF STRENGTH (Psi) DEVELOPMENT IN CONCRETE

Specimens: 3- by 6-in. concrete cylinders.
Aggregate: Elgin, Illinois gravel and rim-developing Jeffersonville limestone from Indiana.
¾-in. maximum size of aggregate.
Nominal cement content: 6.5 bags per cu yd.
Water-cement ratio: 4½ gal per bag. Slump 1-2 in.
Curing: 1 day in molds at 73 F, 100% R.H. then to designated storage.
Each value represents the average of three specimens, one from each of three rounds.

Test Age	100 F over Water		73 F, 100% R.H.		Cycle 2 Days in H_2O at 73 F 5 Days in Air, 100 F, 24% R.H.	
	Jeffersonville	Elgin	Jeffersonville	Elgin	Jeffersonville	Elgin
7 days	6380	5760	5800	5700	5920	5220
28 days	6320	7190	7280	7060	7890	7750
90 days	6040	8790	6950	8350	7870	8300
180 days	6270	9750	6630	8320	7770	9220
1 year	6810	10070	5840	8700	9360	9740

developing rocks, probably because of their lower clay content, tend to be of a higher physical quality than the expansive rocks.

Mechanisms of Reactivity

Extensive chemical studies have been carried out by Bisque and Lemish (11), Harwood and Lemish (12), and Hadley (4) to determine the redistribution of chemical components which causes or accompanies the development of reaction rims on the reactive aggregate particles in concrete. A series of experiments was performed by Hadley (4) in which 1½- by 6-in. cylinders of the reactive rocks were imbedded in a jacket of neat cement paste and moist cured for periods of up to 18 months. The composite paste-rock cylinders were then centered on a lathe and samples turned off at narrow intervals through the paste and then through the rock. A typical analysis is given in Table 3 and the results of the various studies for the individual chemical components are summarized in the following:

TABLE 3

RESULTS OF LATHE EXPERIMENT

Mean Distance from Center of Bar (in.)	Composition by Weight (%)							
	On Ignited Basis							Dried at 110 C
	SiO_2	R_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	CO_2
(a) Original Rock								
—	4.19	1.34	58.97	34.44	0.16	0.21	nil	81.47
(b) Original Paste								
—	20.34	8.23	67.66	0.88	0.21	0.41	1.79	0.32
(c) Paste								
1.662	21.00	8.60	67.21	1.36	0.14	0.28	0.97	9.98
1.500	20.39	8.15	67.84	1.18	0.09	0.10	1.91	1.57
1.250	20.41	8.17	67.88	1.13	0.10	0.10	1.86	0.70
1.000	20.42	8.22	67.80	1.26	0.10	0.11	1.84	0.88
0.750	20.39	8.15	67.78	1.11	0.10	0.12	2.00	0.31
0.700	20.42	8.05	67.88	1.04	0.11	0.13	2.06	0.83
0.650	20.38	8.13	68.34	1.18	0.18	0.25	1.34	3.09
0.640	20.59	8.26	68.10	0.76	0.22	0.27	1.95	2.95
0.630	20.67	8.37	66.95	0.10	0.39	0.58	1.81	12.07
(d) Rock								
0.623	5.00	1.53	57.38	32.79	1.71	1.58	nil	76.78
0.611	4.77	1.35	58.72	33.29	0.67	0.95	nil	79.95
0.597	4.52	1.41	58.82	33.63	0.49	0.70	nil	81.24
0.581	4.33	1.38	59.02	33.66	0.38	0.55	nil	80.34
0.567	4.14	1.29	59.58	34.16	0.48	0.34	nil	81.37
0.550	4.04	1.24	59.70	33.54	0.40	0.28	nil	79.54
0.500	3.83	1.19	60.31	33.06	0.23	0.15	nil	79.32
0.400	3.31	1.32	59.93	33.65	0.09	0.09	nil	81.32
0.300	3.22	1.17	60.31	34.16	0.08	0.09	nil	83.62
0.194	3.50	1.25	59.88	34.39	0.09	0.09	nil	83.26

1. Silica. Studies by Harwood (13) have shown that silica can migrate either into or away from the paste-aggregate interface depending upon the overall mineralogical character and texture of the rock. Hadley has found, however, that in the case of rocks which develop prominent, acid-resistant rims, there appears to be a movement of silica into the rim zone.

Silicified reaction rims derive silica from cement paste (11). Lemish (14) concludes that the principal sources of silica are quartz particles within the rim zone and in some cases, siliceous fine aggregate. There is apparently no contribution of silica from the cement paste. Studies by Hadley (4) suggest that the rims derive silica from the argillaceous and siliceous materials within the rock itself, and that in many cases silica "gradients" are set up which involve the entire aggregate particle.

2. Sodium and potassium. Although Bisque and Lemish (11) found no increase in concentration of alkalies in the rim zone, many of their studies involved soaking of the test specimens; consequently the leaching of the alkalies from the specimens could have been extensive. Studies by Hadley (4) showed a definite increase in concentration of alkalies in both the paste and the aggregate at the interface region.

3. Carbonate. X-ray diffraction studies by Hadley (4) have shown that extensive dedolomitization takes place in the rim zone. The alkali carbonate produced diffuses into the cement paste where it reacts with the hydrated paste to form calcium carboaluminate.

4. Calcium and magnesium. There appears to be no major movement of these elements, although in some instances calcium hydroxide is thought by Lemish (14) to be present in the rim zone.

5. Sulfate. There is a slight accumulation of sulfate ion in the interior of the paste.

Analysis of Possible Mechanisms for Silica Fixation in Rim Zone.—It was postulated by Bisque and Lemish (9) that silicified reaction rims were formed by polymerization of silica on the surfaces of interstitial clay minerals. Supporting evidence was found in the fact that rims could be formed by placing samples of reactive rocks in dilute sodium-silicate solutions or exposing the rock to an atmosphere of silicon tetrachloride or organic silanes.

Although a mechanism of silica polymerization on clay minerals is not unreasonable and may well occur in natural geologic environments, it is felt that the high pH of the concrete environment largely precludes the large-scale polymerization postulated. An experiment was performed in which illite, montmorillonite and kaolinite clays were individually agitated with sodium-silicate solution (0.75M Na_2O, 0.33M SiO_2) for three weeks. Analysis of the solutions showed that rather than removing silica from solution, all of the clays tested were actually somewhat soluble and the silica contents of the solutions were increased (Table 4).

TABLE 4

COMPARATIVE SOLUBILITY OF CLAY MINERALS IN SODIUM SILICATE SOLUTION AND EFFECTIVENESS OF BRUCITE IN REMOVING SILICA FROM SOLUTION[a]

Absorbate	SiO_2 in Sol. (gm/gm of sol.)
Initial sodium silicate solution[b]	0.0210
Montmorillonite	0.0233
Illite	0.0219
Kaolinite	0.0213
Brucite	0.0157

[a] 4 grams absorbate in 40 ml of solution for 21 days.

[b] 0.75M NaOH, 0.33M SiO_2.

Another possible mechanism for the fixation of silica within the rim zone is the precipitation of silica by the brucite formed in the dedolomitization reaction. A sample of brucite was therefore treated with sodium silicate solution as in the previously described experiment. Inspection of the test data, which are given in Table 4, shows that there was a definite silica uptake by the brucite.

On the basis of what is now known concerning the chemistry of rim development and the petrography of the affected concrete, the following sequence of events would appear to best explain the observed development of reaction rims in concrete:

The alkalies released by cement hydration diffuse into the rock where they react with the dolomite, forming brucite and releasing alkali carbonates into solution. The siliceous components of the rock are concurrently attacked by the alkalies, and soluble alkali-silicates are formed. The silicate ion in solution reacts rapidly with the brucite, forming magnesium silicates or magnesium silicate hydrates. The accumulation of these reaction products at or near the interface causes the acid-resistant "reaction rim" to form. As the result of the removal of the silica from solution by the brucite, a silica gradient is set up in the solution phase in the rock which results in a net migration of silica to the interface region.

Meanwhile, the alkali carbonate produced by the reaction of the dolomite diffuses into the paste where it reacts with the calcium sulfoaluminate hydrates, with the resultant formation of the calcium carboaluminate hydrate. The sulfate ion released by this reaction appears to diffuse further back into the paste ahead of the advancing "carbonate front," while the alkalies are regenerated and diffuse again into the rock.

Rocks Which Develop "Negative" Reaction Rims

Mather and Buck, and Newlon and Sherwood (personal communications), as well as the author have found in independent studies that certain fine-grained, low insoluble residue, low dolomite or even non-dolomitic rocks will develop what may be termed "negative rims" in concrete; i.e., peripheral zones which are more susceptible to acid etching than the interior of the rock. If the formation of acid-resistant silicified rims is largely due to a reaction between the brucite formed by dedolomitization and silica derived from the silica-bearing minerals in the rock, the formation of these negative rims is readily explainable. In rocks of this type, containing little or no dolomite, there will be little or no brucite formed. Consequently, the silica in solution in the pore fluids of the rock will not be precipitated in the rim zone, but will be free to migrate completely out of the rock and to react with the cement hydration products. This removal of interstitial silica apparently has the effect of "ungluing" the carbonate grains and renders the periphery of the rock more soluble to acid. There is no evidence that this represents a deleterious reaction in concrete and the introduction of silica into the paste near the interface may in fact be a beneficial reaction.

Tests for Recognition of Rim-Developing Rocks

1. Petrographic examination. The criteria for the petrographic identification of potentially reactive rocks of this type are essentially the same as those for the expanding rocks. The major differences between these two types of reactive rocks are that the rim-developing rocks have a more tightly knit carbonate structure with a high degree of interpenetration of the dolomite crystals, contain less interstitial clay, and tend to be more highly dolomitic.

2. Imbedded cubes. A relatively rapid test for rim development can be made by imbedding ½-in. cubes of rock in 1- × 1- × 11¼-in. mortar bars made with silica sand and a cement of high alkali content. The mortar bars are stored for 8 weeks in cans over water at 100 F. At the end of the storage period the bars are cut in half longitudinally with a diamond saw and etched with dilute hydrochloric acid. The presence of acid-resistant reaction rims is determined by visual examination of the etched bar. A typical test specimen is shown in Figure 12. Similar tests have been used by Bisque and Lemish (10).

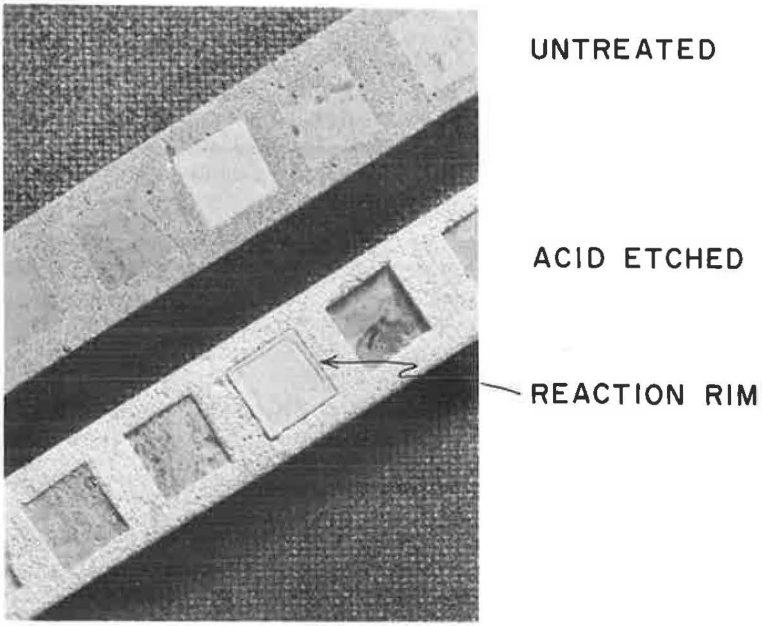


Figure 12. Rock cubes embedded in mortar bars. Development of reaction rims revealed by acid etching of bars.

3. Concrete tests. The effect of rim-developing rocks on the rate of strength development can be checked by compressive strength determinations on concrete cylinders made with reactive rocks and high alkali cement.

Possible Remedial Measures.—Although the exact mechanism by which rim-developing rocks could adversely affect concrete performance has not been established, information at hand would suggest that some reported failures of field concrete might in some way be related to the influence exerted by rim-developing rocks on the rate of strength development.

Preliminary and unpublished studies by Hadley indicate that neither pozzolanic replacements nor use of low alkali cement are effective in controlling this loss of strength. In very recent studies it has been found, however, that detrimental changes in the rate of strength development are at least delayed by the addition of lithium chloride.

RELATIONSHIP BETWEEN RIM-DEVELOPING AND EXPANSIVE ROCKS

Field studies in Indiana have shown that rim-developing and expansive rocks are often found in the same formation and are in fact often interbedded. Much of the Kingston limestone, the "type" rock for expansive behavior, both expands and develops rims, and a portion of the Cedar Valley limestone of Iowa, the classic rim-developing rock, is highly expansive. The two types of rock appear to be closely related, and this portion of the paper attempts to show the relationship between the two types and outlines briefly the factors believed to determine the type of reactivity which a rock would exhibit in concrete.

As previously mentioned, the major difference between rim-developing and expansive rocks appears to be one of clay content. Figure 13 shows the clay contents and carbonate compositions of the highly reactive rocks from Indiana studied by Hadley. The dashed line apparently represents a critical clay content; highly expansive rocks all contained more than this critical amount of clay, whereas the great majority of rim-developing rocks contained less. Certain of the highly expansive rocks also developed

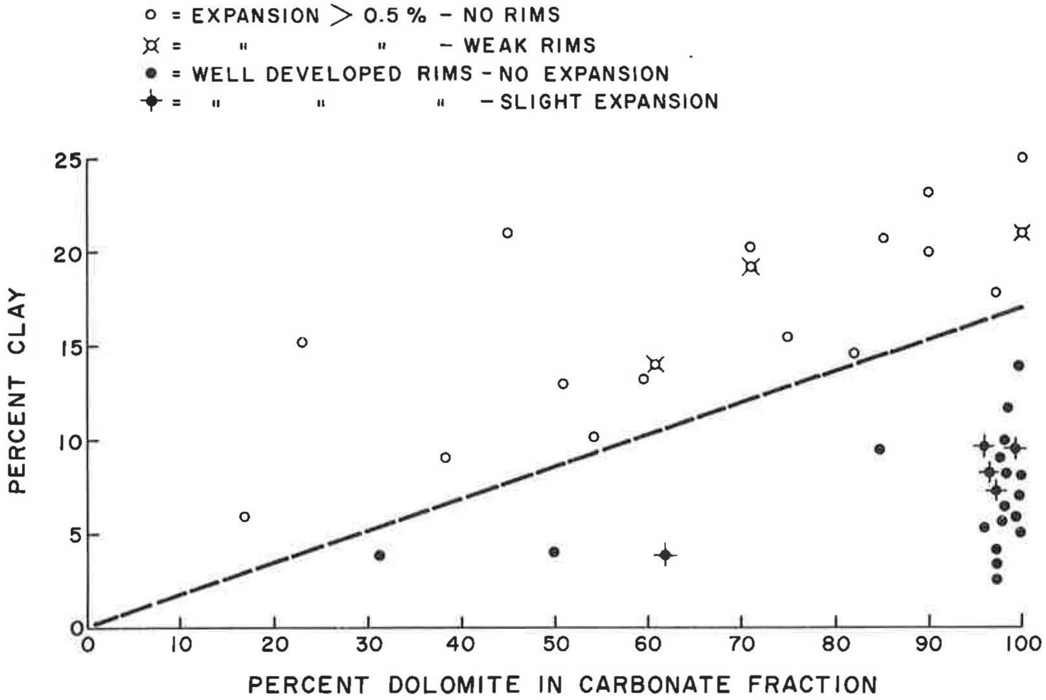


Figure 13. Rim development and expansion are closely related. Type of reactivity shown by a rock is a function of both clay content and carbonate composition.

weak rims and some rim-developing rocks expanded slightly in alkali. These rocks are apparently transitional between the two types.

As the amount of calcite in the rocks increases, highly expansive behavior develops in rocks containing progressively smaller amounts of clay. This is apparently the result of the accelerating effect of calcite on the reaction of the dolomite. As the calcite content increases, the expansive forces generated through dedolomitization show a similar increase. If the dashed line in Figure 13 is interpreted as representing the clay content at which the carbonate skeleton of the rock has been sufficiently weakened through dilution with clay that it can no longer effectively resist the expansive forces within the rock, it seems only logical that as these expansive forces increase, the clay content necessary for expansion shows a corresponding decrease.

It appears that expansion and rim development are both ultimately attributable to the reaction of dolomite with cement alkalies, and that the type of response shown by an alkali-reactive rock depends on both the clay content and the composition of the carbonate portion of the rock.

In highly dolomitic rocks with a sufficiently high dolomite surface to allow significant reaction with alkalies and with a relatively low clay content, the forces generated through the dedolomitization process may be insufficient to overcome the restraint of the rock's carbonate skeleton and dedolomitization then proceeds without the occurrence of expansion. Dissolved silica reacts with the brucite produced by dedolomitization in the rim zone, and alkali carbonates migrate into the paste. Any adverse effects in the concrete are not apparent until appreciable carbonation has taken place. The results attributed to this type of reactivity did not become evident in Iowa pavements until after 5 to 15 years of service.

In rocks which contained more reactive calcite-dolomite mixtures and/or larger amounts of clay, the expansive forces are sufficiently strong to overcome the restraint of the carbonate skeleton and dedolomitization is accompanied by expansion of the rock and a rapid disruption of the concrete. The same chemical processes are involved in both types of reactivity, and given sufficient time, the paste surrounding the expanding aggregate particles would be affected in the same manner as with rim-developing rocks. However, due to extremely rapid disruption of the concrete as a result of expansion of the aggregate, the carbonation of the paste would cease to be a significant factor.

SUMMARY

Although the great majority of dolomitic aggregates gives excellent service in concrete, recent studies have shown that certain classes of fine-grained, argillaceous, dolomitic aggregates can participate in deleterious cement-aggregate reactions. Carbonate rocks known to react chemically in concrete can, for convenience, be divided into two main types: (a) rocks which expand in alkaline environments, and (b) rocks which develop silicified reaction rims in concrete.

The reactivity of both of these rock types is believed attributable in whole or in part to a reaction between cement alkalies and the mineral dolomite. The reaction can be written:

$$\mathrm{Ca\,Mg(CO_3)_2 + 2M\,OH \rightarrow M_2CO_3 + Mg(OH)_2 + CaCO_3}$$

in which M = Na, K, or Li.

This reaction produces appreciable expansive forces within reactive rocks and if these forces are sufficiently strong to overcome the restraint imposed by the carbonate skeleton of the rock, a rapid expansion of the aggregate, and subsequently the concrete, will occur.

In rocks in which the carbonate skeleton has sufficient strength to resist the expansive forces, dedolomitization will proceed without expansion. Instead, reactivity in concrete will be characterized by gradual carbonation of the paste, and if sufficient silica is available within the rock, the development of silicified reaction rims.

Although much remains to be learned before a real understanding of all facets of the alkali-carbonate rock reactions can be reached, considerable progress has been made. Simple test methods have been developed which permit rapid identification of expanding rocks and indicate their general level of reactivity. The behavior of field and laboratory concretes made with these rocks has been established, and the major factors which influence this behavior have been determined. Using this knowledge, several methods for minimizing concrete expansion have been developed and evaluated.

The expansive rocks themselves have been characterized on the basis of mineral composition and texture, and considerable progress has been made in determining the chemistry of this type of alkali-carbonate reactivity. Future research should probably be aimed at determining the exact mechanisms of expansion and the development of true remedial techniques which would permit the safe utilization of the highly reactive rocks as concrete aggregate.

Much has been learned concerning the nature of rocks which develop reaction rims and the chemistry of rim development. The greatest need for future research appears to be the establishment of correlations between rim development and field service records, and the study of those rocks which adversely affect concrete strength.

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Appendix A

QUANTITATIVE CHEMICAL STUDY OF KINETICS OF DEDOLOMITIZATION REACTION

To study in detail the factors which influence the kinetics of the reaction of dolomite, a series of experiments was performed in which prepared mixtures of calcite and dolomite were reacted with various solutions of the alkali metal hydroxides. The amount of dolomite reacted was estimated from the amount of carbonate ion released into solution. Details of these experiments are given below.

Materials

The materials used were a reagent grade calcite and a well-crystallized dolomite of almost ideal composition. Analyses of these minerals were

Percent by Weight

	CaO	MgO	CO_2
Dolomite	30.71	21.57	47.46
Calcite	55.21	00.24	43.78

The minerals were hand-ground in a mullite mortar and screened into the desired size gradations.

Solutions of the alkali metal hydroxides were prepared taking every precaution to avoid carbonation. Fresh solutions were prepared for each experiment, and each solution was analyzed for carbon dioxide. The CO_2 (carbonate ion) content of most of these solutions was less than the minimum amount detectable (0.03 percent) by the analytical methods used. Only as much as 0.04 percent CO_2 by weight was detected in isolated cases.

Experimental Procedures

The experimental techniques used were of two types. In the early studies, such as reported by Hadley (4) and reproduced in part as Figures 4 and 5 of this paper, 5-gm samples of various mixtures of calcite and dolomite were placed in small polyethylene bottles, 20 ml of 1M NaOH solution was added, and the bottles were immediately closed and sealed with wax. The bottles were then placed on a rotating wheel and the mixtures allowed to react for 14 days. Duplicate tests were made in all cases.

After 14 days the samples were filtered rapidly in a CO_2-free atmosphere. The filtrates were placed in small polyethylene bottles which were then sealed with wax pending analysis. Typical results are shown in Figures 5 and 6.

In later studies, the results of which are summarized in Table 1 of this paper, the weight of dolomite and of sodium hydroxide were held constant in all samples. Variations in calcite-dolomite ratio were brought about by successively larger additions of calcite to a constant amount of dolomite (4 grams). Variations in the concentration of the solutions were similarly brought about by successive dilutions of the initial sodium hydroxide solution. For example, in three cases, 45 ml of 1M NaOH, 90 ml 0.5M NaOH and 900 ml 0.05M NaOH were used.

Aside from these variations in composition, the procedures were the same as those outlined for the first series of experiments.

The determinations of the carbon dioxide contents of the alkali solutions were made by an evolution procedure. In the apparatus[1], nitrogen gas is used to carry the CO_2, liberated by acid and heat, into a weighing tube containing ascarite and anhydrous magnesium perchlorate. Copper sulfate was not used in the train, and sulfide sulfur would interfere, if present. No accuracy was lost as the materials used did not contain sulfide.

Accuracy of Determinations

Accuracy of the determinations could be affected by gain or loss of carbon dioxide to the atmosphere, by the carbonate content of the original alkali solutions, and by release of carbonate ion from the calcite under the action of the strong alkali. Corrections necessitated by these factors were carefully investigated. The effect of the carbonate content of the solutions has already been discussed.

The fact that the carbonate ion in solution was released almost entirely by the dolomite was demonstrated in several ways. Samples of calcite equal in weight to those used in each of a series of tests of calcite-dolomite mixture were treated individually with samples of the same sodium hydroxide solution under the same conditions and for the same reaction period, and the carbonate ion released into solution was measured. In other instances the "blanks" were made only on the maximum weight of calcite used in a given series of tests. The values of the corrections ranged from 0.00 percent to 0.13 percent and were significant only in instances where very little reaction occurred, because the total carbonate contents of highly reactive mixtures ranged as high as 1.75 percent. The large number of instances in which the blanks had a carbonate content below the range of the analytical method indicates that the corrections can be attributed almost entirely to atmospheric contamination. In an additional demonstration, it was determined from X-ray diffraction patterns of samples before and after alkaline treatment that the dolomite rather than the calcite had reacted.

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[1] See, for example, p. 236 of "Scott's Standard Methods of Chemical Analysis," Vol. 1, Fifth Edition, D. Van Nostrand (1939); p. 768 of W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," Second Edition, Wiley (1953); or p. 325 of F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2, Ninth English Edition, Wiley (1948).

Appendix B

PRELIMINARY STUDIES OF OSMOTIC PHENOMENA ASSOCIATED WITH EXPANSION OF ALKALI-REACTIVE DOLOMITIC ROCKS

Introduction

Although relatively good correlations have been established between the reaction of dolomite and the expansion of alkali-reactive carbonate rocks, certain aspects of the problem have remained unexplained. One of these is the magnitude of expansion shown by the more reactive rocks. The slow and relatively small expansion (0.15 percent in 100 days), which was measured for a single dolomite crystal, does not seem adequate to explain the expansions of close to 5.0 percent measured in rocks after only 7 days in alkali. The role of clay in the expansion of these rocks is also an enigma, as it has been found that expansion will occur only with rocks in which the individual dolomite crystals are largely surrounded by the clay matrix. Numerous explanations could be put forward to explain the expansion of the clay itself, but all experimental evidence has shown that expansion will take place only when finely divided dolomite is present. A series of experiments was therefore initiated to study possible interactions between the clay and dolomite fractions of alkali-reactive carbonate rocks. As one phase of this study, experiments were performed to explore the possibility of osmotic effects involving clay or clayey limestone membranes.

Apparatus

Tests were run using osmotic test cells such as described by Verbeck and Gramlich (15). In place of the cement paste membranes used by Verbeck, membranes of remolded clay or clayey limestone were used. These are described as follows:

Clay Membranes.—Raw Fithian illite, was air-dried and ground to pass a 200-mesh screen. Water was then added until the material was sufficiently plastic to be workable. The moist clay mass was sealed in a polyethylene bag and aged in the moist room for 14 days. The clay was then placed between two sheets of plastic film and rolled out with a rolling pin to a thickness of ½ in. A series of membranes 2 in. in diameter was cut from the sheet with a razor blade and stored over water in a sealed container until used.

Rock Membranes.—A series of rock membranes 2 in. in diameter and ½ in. thick were cut, using a diamond saw from a rock which was a very homogeneous argillaceous dolomitic limestone from the Mississinewa shale (Silurian) of Indiana. The rock contained 16 percent acid-insoluble residue, and 20 percent of the carbonate fraction was dolomite.

Each of the following experiments was repeated at least twice with each type of membrane:

Test 1.—One chamber of the cell contained 1M NaOH, the other an equivalent amount of 0.5M $NaCO_3$ solution. This system represents the concentration relationships which would presumably be present in a reacting rock.

Results.—A very rapid flow took place into the side of the cell containing the $NaCO_3$ solution with both types of membrane.

Test 2.—Five grams of dolomite ground to pass a 400-mesh screen were placed in one chamber of the cell. Both chambers were then filled with 1M NaOH solution.

Results.—There was an initial flow away from the dolomite, followed by a reversal and eventual rapid flow into the chamber of the cell containing the reacting dolomite with both types of membrane.

CONCLUSION

On the basis of these experiments, it seems possible that the expansion of the reactive carbonate rocks might be largely attributable to osmotic forces centered at the reacting dolomite crystals and operating through the interstitial clay-carbonate matrix.

Discussion

MICHAEL A. OZOL, Highway Materials Research Analyst, Virginia Council of Highway Investigation & Research—Hadley, in discussing the factors influencing the reaction rate of dolomite, shows that the degree of acceleration is a direct function of the amount of the admixed calcite (Fig. 5). He further states that: "While the percentage of (the dolomite fraction—MAO) reacted in calcite-dolomite mixtures is greatest for the mixtures highest in calcite, the relationship between rate of reaction and the amount of dolomite available for reaction is such that the greatest amount of dolomite is reacted in mixtures containing approximately equal amounts of calcite and dolomite (Fig. 6)."

This experimental observation, that the acceleration of the dedolomitization reaction by calcite results in a maximization of the total amount of dolomite obtained, or reacted, at the 50-50 proportion, may be supported by a simple mathematical observation.

The relationship is that the rate of dedolomitization is increased in proportion to the amount of calcite present. But, as the amount of calcite increases, the proportion of dolomite decreases. Therefore, although the rate of reaction increases with the percent of calcite, there is always less dolomite present so that the resulting total dolomite reacted, first increases—to a point—then decreases. For purposes of illustration assume a 100-gm sample varying from 0 to 100 percent calcite (inversely 100% to zero dolomite). Also, assume that the percent of the dolomite fraction reacted will be 0.001 of the percent of calcite present in the calcite-dolomite mixture. Table 5 and Figure 14 illustrate the relationship. It may be seen that the curve obtained from plotting the figures (amount dolomite reacted vs percent dolomite in mixture) is symmetrical about the 50-50 proportion and is, in the writer's view, the theoretical explanation for that shown in Figure 6.

TABLE 5

CALCULATION OF AMOUNT DOLOMITE REACTED

A	A'	B	C = B × A
Dolomite (%)	Calcite (%)	% of Dolomite Fraction Reacted 1/1,000 of Col. A'	Amount Dolomite Reacted (gm)
100	0	0	0
90	10	0.01	0.9
80	20	0.02	1.6
70	30	0.03	2.1
60	40	0.04	2.4
50	50	0.05	2.5
40	60	0.06	2.4
30	70	0.07	2.1
20	80	0.08	1.6
10	90	0.09	0.9
0	100	0.10	0

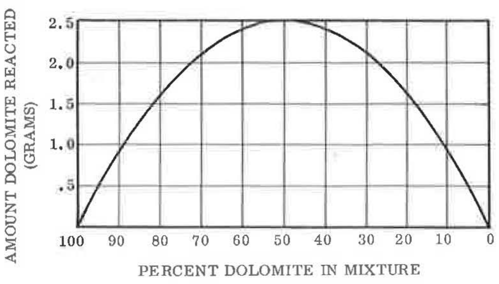

Figure 14. Amount dolomite reacted vs percent dolomite in mixture.

Alkali-Carbonate Rock Reaction

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This paper constitutes a review of eight years of research on the alkali-carbonate rock reaction by the Division of Building Research, National Research Council, Ottawa, Canada. Most of the material has been, or will be, published elsewhere. A summary is given of the original Kingston case which first revealed excessive expansion in concrete resulting from alkali-carbonate reactivity in a dolomitic limestone coarse aggregate. Further field studies are described, as well as investigations into the nature of the reaction, methods of test and identification, and some hypotheses concerning the mechanism of reaction and expansion.

•THE expansive type of alkali-carbonate rock reaction in concrete has now been established as a phenomenon quite distinct from the better known alkali-silica reaction. It appears to be limited to certain fine-grained, argillaceous, dolomitic limestones when these are used as coarse aggregate. The rate and extent of the expansion of the concrete increases with increase in alkali content of the cement, and the reaction requires the presence of moisture.

Since the first publications on the alkali-reactive carbonate rock at Kingston, Ontario, by the present authors (1, 2), problems with limestone aggregates in other areas have been re-examined. Some of these have been identified with the alkali-carbonate rock reaction, the most extensive studies being those of Hadley (3) and Newlon and Sherwood (4). A less clear-cut but apparently related type of reaction occurs with carbonate rocks in Iowa, as reported by Bisque and Lemish (5, 6, 7) and Lemish, Rush, and Hiltrop (8).

Although the actual mechanism of the expansive reaction involving carbonate rock is still being debated, much has been learned about the compositional and environmental factors involved. Methods of identification and testing have been developed, remedial measures have been determined (9), and some progress has been made in applying these to specifications and practice in the Kingston area.

Fortunately, the occurrence of expansive carbonate rock appears to be relatively rare, and confidence in the use of limestones and dolomites as concrete aggregate is not impaired. Nevertheless, the evidence now available indicates that in affected areas the problem is of much more than academic interest.

This paper represents a summary of the studies carried out by the Division of Building Research on this reaction. It deals with investigations concerning (a) the solution of the practical problem in Kingston, (b) the nature of the reaction, (c) methods of test and identification, and (d) possible mechanisms. Most of the test results shown have been taken from reports published elsewhere by the authors, the references being given in each case.

STUDIES DIRECTED TO THE FIELD PROBLEM

The Barriefield Case

In the fall of 1955 the Division was asked by Defence Construction (1951) Limited to investigate unusual cases of growth and cracking of recently placed concrete at Barrie-

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Paper sponsored by Committee on Performance of Concrete—Chemical Aspects.

field, site of a large army establishment on the outskirts of Kingston, Ontario. The most dramatic evidence of expansion was in sidewalks and curbs where joints closed up, concrete buckled, and map-cracking occurred (Fig. 1). The fact that this took place within the frost-free season suggested some type of cement-aggregate reaction, and this line of investigation was followed from the beginning.

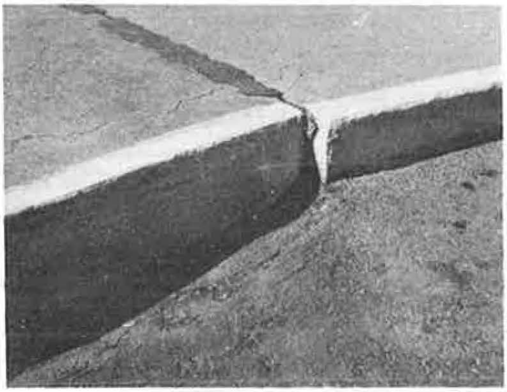


Figure 1. Expanding concrete resulted in closing of joints, buckling, and map-cracking.

First tests consisted of making concrete prisms using job materials and mix designs, and exposing these to continuous fog-room conditions. Expansions of 0.1 percent and cracking occurred within six weeks. Similar tests were made using low alkali cement as well as the local high alkali cement normally supplied in this area. The rate and degree of expansion increased with increasing alkali content of the cement (Fig. 2). Extensive tests with various combinations of different coarse and fine aggregates revealed that the dolomitic limestone coarse aggregate was the expansive component. Thus, from the start of the investigation, it was clearly evident that an alkali-aggregate reaction was involved.

Concurrent with these tests, the aggregates were subjected to standard ASTM acceptance tests. On this basis the "reactive" coarse aggregate could be classified as satisfactory for concrete. Also, concurrently, the aggregates were tested for reactivity according to ASTM methods. Although abnormal expansion occurred in the mortar bar test (ASTM Specification C227), it could not be classified as excessive on the basis of the then accepted limits (1). Pozzolan and chemical inhibitors, which had proved effective for reducing expansion in concretes made with other alkali-reactive aggregates, were not effective in this case, as shown by tests over a 2-yr period (2). It was also noted that affected concretes did not show evidence of the gel exudations normally associated with the alkali-silica reaction, and "rim formations" on aggregate particles were fewer and different in appearance.

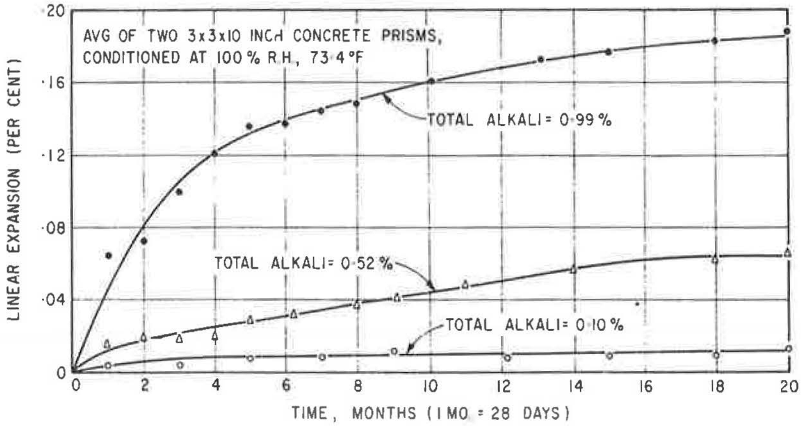


Figure 2. Reactive coarse aggregate in concrete produced expansion according to content of cement alkali.

At the outset, the Division sent samples to the Bureau of Reclamation and the U.S. Corps of Engineers for expert petrographic examination. It was concluded from observations of Mielenz, K. Mather and B. Mather that some sort of cement-aggregate reaction was involved but that it was an unusual type not previously experienced. The Division was fortunate in having continuing access to supporting evidence from similar studies by the Portland Cement Association which initiated work on the Kingston rock only a few months after the investigations in this laboratory were begun, and whose first published results by Hadley appeared later (3).

In early 1957, the Division made tentative recommendations for Kingston construction agencies to use a cement of sufficiently low alkali content, or obtain non-reactive aggregates from other sources.

Field Concretes in the Kingston Area

The Division of Building Research made extensive field studies and observations at the beginning of the investigation and selected cases have been followed to the present date. As with other problems of this type, such observations were not only fruitful in characterizing the phenomenon as a supplement to laboratory experiments, but were essential in clarifying the local situation which was inevitably fraught with conflicting interests and preconceived opinions. From a mere superficial examination of field concrete, one might have concluded that the problem was not extensive, and that much of the evidence was contradictory. Detailed examination, however, and care in obtaining reliable information as to kinds and sources of materials, methods and practices followed, and environmental history, invariably supported experimental results and showed clearly the wide occurrence of the phenomenon in the Kingston area.

The most dramatic and clear-cut cases of excessive expansion were found in exposed slabs on ground where differential movement had occurred due to difference in moisture environment between the top and bottom surfaces. This has produced the now familiar pattern cracking in sidewalks, floors, exposed footings, and loading platforms (Fig. 3).

Where moisture conditions have been relatively uniform, or where the concrete elements were thick or of low surface area to volume ratio, excessive expansion is evidenced by closing of joints and extrusion of joint filler (sidewalks), buckling (curbs, floors), and cracking in rendering or brick superstructure.

An interesting feature of affected, exposed concretes that have resisted other environmental factors over many years, is that the concrete sections within the crack boundaries are essentially intact and the edges at the cracks have remained sharp (1, 2).

Special study was made of many cases where no evidence of excessive expansion had occurred. Almost without exception, this was found to be due to the absence of coarse aggregate, as in some repair toppings on sidewalks; the presence of a low proportion of coarse aggregate of small maximum size; or the use of non-reactive stone. In some instances, expansion had been retarded by early drying, as in slender bridge railings.

Basement and garage floors were at first exhibited as contradictory evidence

Figure 3. Typical pattern cracking in sidewalk in Kingston.

inasmuch as cursory observation revealed no cracking. When these were wiped with a damp cloth or flushed with water, the familiar pattern cracking became visible. It was estimated by the Division that at least 70 percent of the concrete in the Kingston area was visibly affected to a greater or lesser extent by this reaction.

Kingston Limestones

Three limestone quarries had been the main sources of coarse aggregate for concrete in the area for many years prior to the start of the studies by this Division. Field evidence showed that rock from all three had been responsible for excessive expansion and cracking of local field concretes. One of the two large quarries, hereafter designated as quarry A, was studied most exhaustively in this laboratory. It had been the source of coarse aggregate in the Barriefield case. Quarry B was also studied in considerable detail. The reactivity of the rock in quarry C, a smaller quarry, mined by the penitentiary in Kingston, was established largely through observations of field concretes.

The variable reactivity of the rocks in quarries A and B is given in Table 1 in terms of expansion of concrete beams. The most expansive rock was the 0- to 24-ft section in quarry A. As coarse aggregate, it had to be classed as physically satisfactory for concrete when evaluated by conventional acceptance tests and specifications accepted at that time. Despite the lower expansive tendencies produced by the rocks in quarry B, laboratory and field evidence showed that failure of concrete occurred when a high alkali cement was used. It is noted that a very low cement alkali is required in the extreme cases to produce an essentially non-expansive concrete. The distribution of rock beds of high, moderate, and low expansivity, makes it virtually

TABLE 1

EXPANSION OF CONCRETE[1] MADE WITH ROCK FROM DIFFERENT LEVELS IN QUARRIES A AND B

Quarry Level (ft)	Cement Alkali, as Na_2O (%)	Linear Expansion (%)			
		6 Mo.	12 Mo.	18 Mo.	24 Mo.
Quarry A:					
0-24	1.19	0.233	—	—	—
	0.36	0.027	0.034	0.045	0.048
24-30	1.19	0.017	—	0.026	0.026
30-36	1.19	0.002	—	0.006	—
	0.36	0.005	0.009	0.010	0.012
36-48	1.19	0.058	0.070	0.087	0.092
	0.36	0.010	0.012	0.016	0.020
48-60	1.19	0.023	0.030	0.033	—
	0.36	0.016	0.008	0.008	—
Quarry B:					
0-12	1.19	0.093	0.110	0.115	0.118
	0.36	0.010	0.018	0.020	0.020
12-13	1.19	0.022	0.032	0.033	0.037
	0.36	0.001	0.006	0.010	0.011
13-48	1.19	0.050	0.050	—	0.060
	0.31	0.014	0.019	0.023	0.026

[1] Prisms, 3 x 4 x 16 in.
Condition: 100% R.H. and 73 F
Mix = 1:2:3¼
Max. size rock = ¾ in.
Slump = 1 in.

impossible to develop selective quarrying in these two particular quarries. In a later section concerned with the nature of the reaction, further consideration is given to variability in reactivity.

Early geological investigations in the vicinity of Kingston were made by the Ontario Bureau of Mines (10) and by the Department of Geological Sciences, Queen's University, Kingston. These indicated that the limestones belong to the Black River Group of the Ordovician System. Following the early studies of the Division of Building Research which revealed the problem of expansion in concrete, more detailed geological work was carried out by Maycock (Department of Geological Sciences, Queen's University, M.S. thesis, unpublished). The petrological results of this study were essentially in accord with the conclusions reached by the Division.

Maycock also investigated the problem of alkali reactivity of the rocks. His results, based on "limited expansion data," disagreed with those obtained in this laboratory only in the magnitude of expansion as recorded on concrete beams.

Recommended Field Practice

The preliminary experiments carried out at the Division of Building Research provided sufficient information to prescribe measures which would permit the continuing use of the local aggregate in the Kingston area (9). Subsequent laboratory studies and field performance have supported these early recommendations.

Laboratory tests showed that expansion of concrete with highly reactive carbonate rock could be reduced to "safe" values only if the alkali content in the cement is below 0.45 or 0.40 percent (total alkali calculated as Na_2O). Thus, the normally accepted maximum of 0.60 percent total alkali in low alkali cement is not adequate for the highly expansive carbonate rock. A special low alkali cement was produced by a cement plant in Ontario for trial use at Kingston. Three cases where concrete was made with this cement and the reactive aggregate from quarry A have been under observation by the Division up to the present (6 years). In each case the concrete has not shown visible signs of distress due to excessive expansion and cracking.

In laboratory experiments, concrete prisms made with the highly expansive limestone and a cement alkali content as low as 0.36 percent (total as Na_2O) have gradually expanded to an excessive extent after two to six years when exposed continuously in a fog room. Partial drying of the concrete after curing has, however, been shown to retard expansion even with the most reactive combinations (Fig. 4). Thus normal field concrete made with cement of sufficiently low alkali content should perform satisfactorily for a full lifetime, except in those special cases where the concrete remains continuously wet.

The durability of concretes made with special low alkali cement was investigated thoroughly, using stone from various beds in quarries A and B. Freeze-thaw tests consisted of 6 hr freezing in air at 18 F and 6 hr thawing in water. After about 3,650 cycles (over a 6-yr period), air-entrained concrete made with the most reactive aggregate and the special low alkali cement showed no measurable deterioration, and compared favorably with reference concrete made with aggregate of good durability history. With high alkali cement the concretes made with reactive aggregate had expanded excessively at about 150 cycles, and showed a sharp reduction in dynamic modulus after about 300 cycles.

Companion samples to these were subjected to wetting-drying cycling similar to the Scholer test (11). Again, the concretes made with expansive aggregate and low alkali cement did not expand excessively after about 500 cycles, whereas the concrete made with the high alkali cements expanded at about the same rate as those exposed in the fog room (2).

Early in the investigation, tests were made to determine the effectiveness of inhibitors normally found effective in reducing expansion due to alkali-silica reaction. Typical results were published in a previous paper (2). Ten pozzolanic materials were selected, one being a well-known California calcined shale. The usual concrete prisms were made with the reactive Kingston carbonate rock as coarse aggregate. The pozzolans were used as a 25 percent replacement of the high alkali cement. Compared

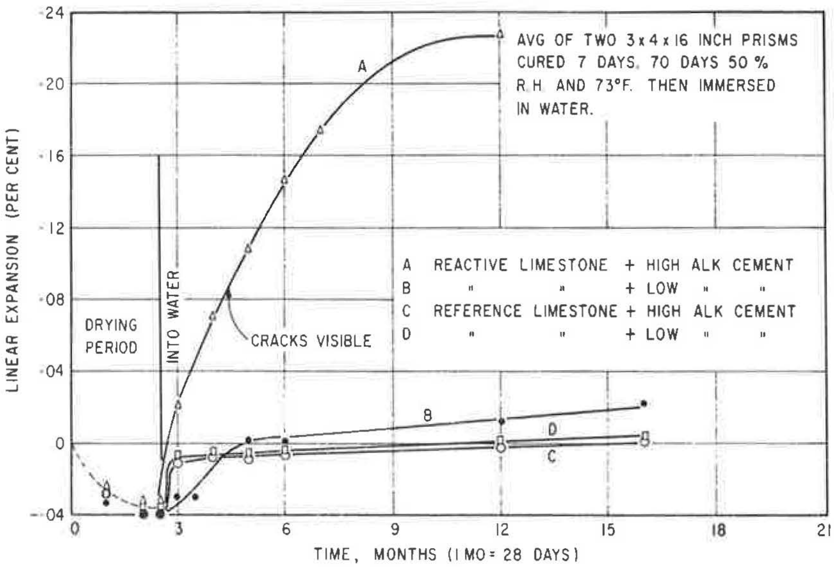


Figure 4. Expansion of test concretes following initial drying period.

with the reference specimens the concrete beams containing pozzolan showed varying degrees of reduced expansion for the first 16 months of continuous moist room storage. At this age the most highly active pozzolans could be considered as effective. At 2 years, however, all expansions had attained the same magnitude. These disquieting results were confirmed by a test using a known chemical inhibitor of alkali-silica reaction, lithium chloride, in which no reduction in expansion occurred at any time up to 2 years.

Mortar bar test results (1) showed that the same calcined shale effected a considerably reduced expansion up to 39 months. Despite this, and because the concrete prism test was considered more direct and realistic, it was concluded that inhibitors normally found effective for alkali-silica reaction could not be relied on to control expansion in the alkali-carbonate rock reaction. It appears that this laboratory is the only one that has reported test results on the effectiveness of pozzolans. Further investigation is obviously needed.

On the basis of these test results, consisting of tests on more than 500 concrete prisms, with observations extending to more than 6 years, the Division recommended that, where the reactive Kingston dolomitic limestone aggregates were to be used in concrete, the alkali content of the cement (calculated as Na_2O) should not exceed 0.40 or 0.45 percent (2, 9). Because laboratory tests had shown that the rate and ultimate extent of expansion decreased with decreasing maximum size of coarse aggregate (2), it was also recommended that maximum stone size be kept to a minimum consistent with good quality concrete. Minimum cement content and minimum coarse aggregate content, also consistent with quality concrete, were recommended. Blending or dilution of reactive aggregate with non-reactive aggregate had been shown to yield expected reduction in expansion. Where possible this was suggested as an additional precautionary measure.

It was further recommended that special attention be given to expansion joints and that provision be made for permitting the concrete to dry out after curing. When carbonate rock aggregate derived from sources other than the quarries investigated, it was urged that it be tested for reactivity before use.

Apart from the trial use of low alkali cement, the extent to which the foregoing recommendations have been practiced in Kingston has not been followed closely. To a very considerable extent, outside aggregates of non-carbonate type are now being used in place of the limestones from the existing quarries. In a recent shopping center development, however, the reactive limestone was used with a high alkali cement, with predictable results: sidewalks show extensive map-cracking.

STUDIES ON THE NATURE OF THE REACTION

Expansion of Concretes

The increase in rate and degree of expansion with increase in alkali content in laboratory concrete made with reactive carbonate rock as coarse aggregate, was found to hold whether all the alkali derived from the cement or whether part of the alkali was added (2). This effect is shown in Figure 5, which may be compared with values in Figure 2. First visual evidence of cracking of 3- by 4- by 16-in. concrete prisms occurred at expansions from 0.04 to about 0.08 percent. It is also seen that the sodium form of the alkali gives a more severe reaction than the potassium form at the higher alkali content.

In making comparisons between the expansion values of the various concrete test specimens described herein, one must bear in mind that the length changes which are measured after cracking has begun, may be greatly influenced by mechanical and other factors not directly associated with the reaction proper. It is therefore desirable to rely mainly on expansion data up to about 0.05 percent. This applies equally to length change information on rock prisms described in a later section.

Tests with 15 cements of varying composition showed that cement components other than alkali appeared to have no significant influence on the expansive properties of the reactive coarse aggregate.

In one series of comparative tests with concrete prisms, the rate and degree of expansion was highest under conditions of wetting-drying cycling (11), slightly less in fog-room conditioning at 73 F, considerably less in freeze-thaw cycling, and lowest in continuous outside exposure. In all cases, however, expansion was excessive and cracking occurred (1). The reaction was obviously affected by variations in moisture and temperature.

In another experiment concrete prisms were cured for 7 days, dried for 63 days at 50 percent relative humidity and 73 F, and then placed in water at 73 F (2). No expansion occurred during the drying period, but rapid expansion followed immersion in water (Fig. 4). These results show the direct dependence of the reaction on moisture.

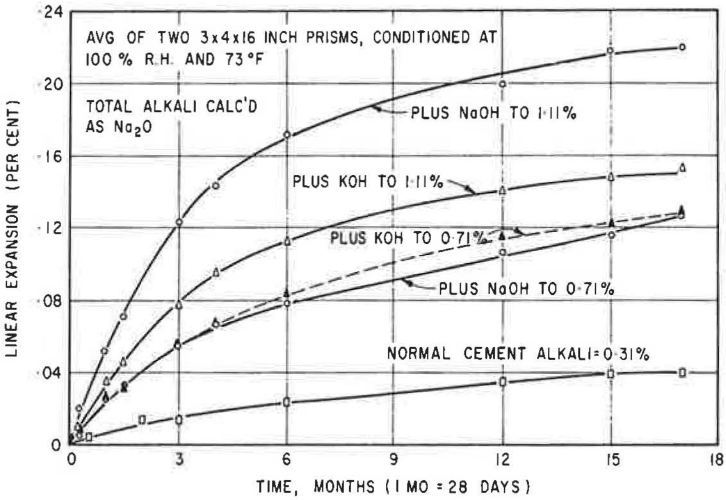


Figure 5. Concrete expansion with reactive carbonate rock and low alkali cement with added alkalis.

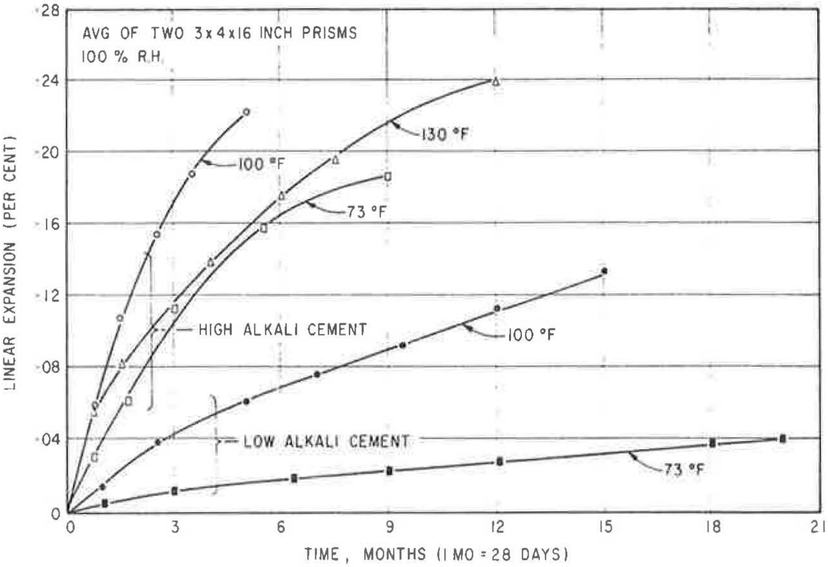


Figure 6. Effect of temperature on expansion of concrete made with reactive carbonate rock.

Similar concrete prisms were conditioned at 73, 100 and 130 F at 100 percent R. H. The highest expansion occurred at 100 F (Fig. 6), at which temperature even low alkali cements produce excessive expansion. These results, discussed in more detail in a previous paper (2), show a certain dependence of the reaction on temperature. These results suggest that the reaction is essentially chemical in nature.

Petrographic examination of concrete made with aggregate from the top 24 ft of quarry A showed that "reaction rims" did not surround all the coarse aggregate particles. At that time it was suspected that rim formation was related in some way to the expansive reactivity. It was therefore concluded that the strata represented in the top 24 ft of quarry A contained beds which differed in reactivity.

Concrete beams were made in which the aggregate was taken from selected beds within the 24-ft section. Test results verified the supposition of varying reactivity as the beams showed different rates of expansion (Fig. 7). This does not necessarily support the postulated relationship, however, between expansive reactivity and rim formation. The nature of the rims has not been established for the Kingston case and further investigation would be required to determine whether a connection exists between rim formation and expansion. Some non-expansive rim-forming dolomitic limestone aggregates in Iowa have been described (7).

Expansion of Carbonate Rock in Alkaline Solutions

Extensive experiments showed that the reactive dolomitic limestones expanded excessively when immersed directly in 2-molar alkaline solutions; the rate and degree of expansion were dependent on concentration of alkali (2). Companion prisms were immersed in water and similarly measured for comparative purposes. These prisms showed no significant expansion. Non-reactive rocks did not expand excessively in strong alkali.

One method consisted of saw-cutting rock prisms of 1½ by 1½ by 5¾ in., planing the ends, and measuring in a mortar bar comparator with adaptor plates for the ends of the prisms. Expansions were of the same order as for concretes containing reactive coarse aggregate (Fig. 8). Similar orders of expansion were obtained by vacuum saturating coarse aggregate with alkaline solutions and measuring the total volume change of aggregate plus solution by means of capillary tubes.

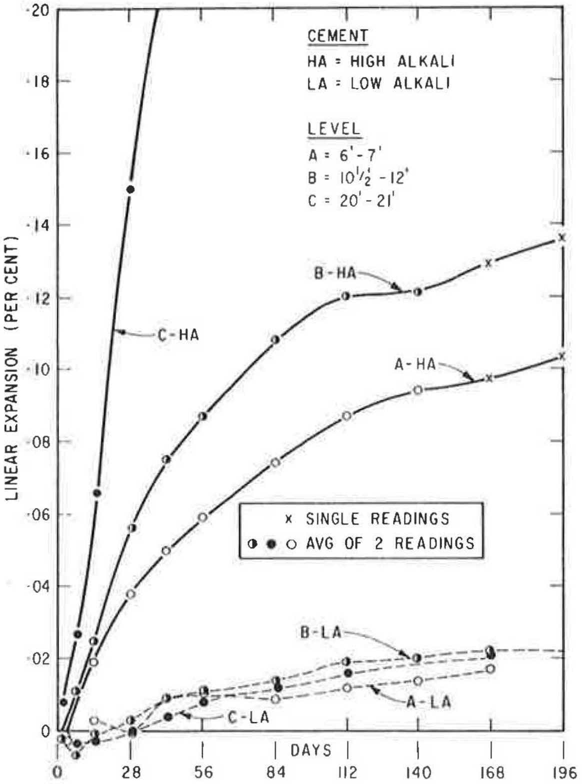


Figure 7. Different expansions in concrete caused by Kingston aggregate from specific strata in quarry A.

Apparatus was developed for measuring expansion of the reactive rock in powdered form (12). This consisted of a cell in which the powdered rock was contained in a compression chamber. The sample was confined under a pressure of 5 lb between a porous plate of stainless steel and a rubber membrane. Volume change was recorded in a 1-mm bore precision capillary tube. The compression chamber communicated via the porous plate with a reservoir. This was filled with water for the initial portion of the experiment until equilibrium was established, and then the water was replaced by 2M alkali. If 100 ml of 2M NaOH and about 30 gm of Kingston rock were employed, the reaction went to completion. A total expansion of more than 7 percent of the initial solid volume was recorded in some instances. Rate and total expansion varied with the particle size of the sample.

Petrography

In the spring and summer of 1958 the authors began a detailed investigation of the petrology of the rocks near Kingston (13). Rocks were obtained at various localities in the area, but sampling was most detailed in the quarries from which the reactive aggregates had been obtained. The rocks are well stratified and there are some beds of the order of 1 ft or so in thickness. The rocks are very fine-grained dolomitic limestones which weather pale to dark grey. Bulk specific gravity was 2.7 and absorption 0.7 percent. There are also certain beds that reach a thickness of about 6 ft, and weather pale green. The dolomite, clay and quartz content is higher in this type of rock. It is also more porous and has a high absorption of 3 percent. Some of the quartz crystals are visible to the naked eye as rounded grains about 1 mm in diameter. The content of $CaCO_3$ (calcite) is low. This greenish rock, which produced only very slight expansion when used as aggregate in concrete, is properly classified as an argillaceous dolomite. The highly reactive rocks, on the other hand, contained more calcite and are correctly described as dolomitic limestones. In these rocks the porosity was about 0.5 percent and the acid-insoluble content was lower than in the greenish rock.

In one quarry specific beds were sampled and the rock used as aggregate for pairs of concrete beams. In each case one pair of concrete beams was made with high alkali cement and an additional pair was made with low alkali cement. The concrete beams were stored at a relative humidity close to 100 percent at 73 F. Rock from different beds, which was quite similar petrographically, caused different rates of expansion in the beams made with high alkali cement (Fig. 8). The reactive rocks, however, were all of a similar petrographic type.

Microscopic thin sections were prepared from the rock in the natural condition, from the rock after soaking in alkali, and from concrete on which large expansions had been recorded.

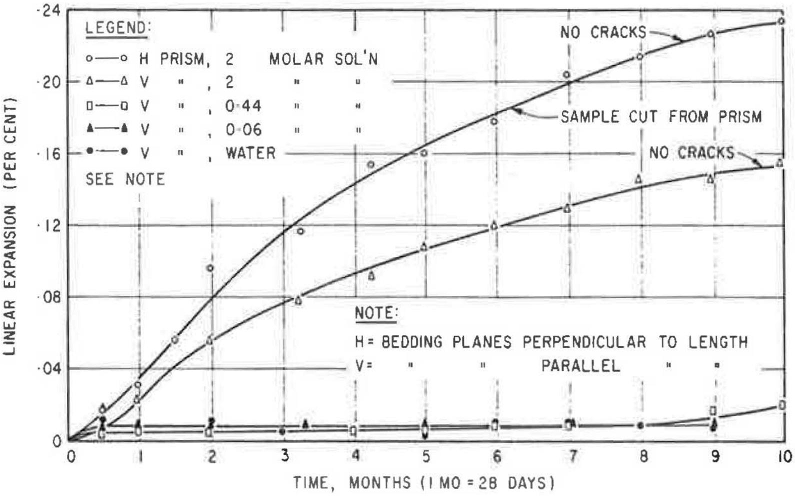


Figure 8. Expansion of reactive carbonate rock prisms in alkaline solutions of different concentrations (6- to 7-ft bed, quarry A).

In the reactive Kingston rocks (Fig. 9) dolomite occurs as well-formed crystals which are generally of rhombic shape and attain a size, at most, of 0.05-mm (50-microns) cross-section. The crystals often contain inclusions of dusky material, which is probably clay, and this is sometimes regularly arranged with respect to prominent crystallographic planes (Fig. 10).

Only a small amount of iron and manganese was found on chemical analysis of dolomite concentrates (13). This makes it unlikely that the included material represents carbonate such as ankerite, ferrodolomite or kutnahorite formed, either by zonal growth upon, or by exsolution from within, the parent lattice. Differential thermal analysis also gave no indication of the presence of ankerite.

The dolomite is of fairly even distribution when the rock is considered on the scale of hand-size specimens, but there is some lack of uniformity on the microscale. Observational evidence shows that the dolomite is not sedimentary and its crystal-

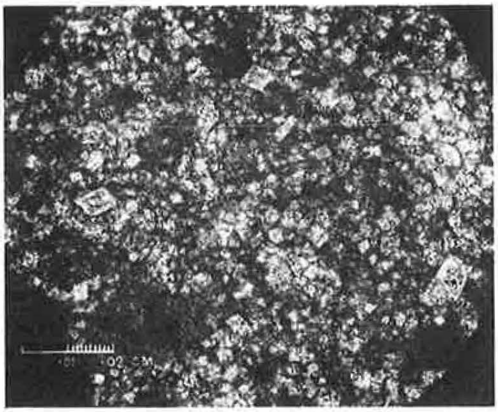


Figure 9. Photomicrograph of alkali-reactive dolomitic limestone, Kingston, Ont.

Figure 10. Photomicrograph of reactive rock from Kingston, Ont., showing dolomite crystal containing inclusions arranged with respect to crystal shape.

lization postdated the deposition of the rock. This dolomitization process was to some extent selective and accounts for the slight lack of regularity in dolomite distribution. During deposition, wave or current action broke up partly consolidated sediment which was then redeposited in quieter water. Thin sheets accumulated of irregular particles, 0.2 to 0.1 mm across, composed of very fine calcite. Space between the particles is often filled with material that contains some larger crystals of clear calcite which petrographic criteria indicate to have formed as a void and pore filling cement. These layers are interbedded with more homogeneous material consisting of micron-sized calcite which appears dusky brown in section under the microscope. It shows little or no sign of recrystallization into larger crystals. This fine calcite is evenly mixed with clay, fine quartz and other tiny crystals of detrital minerals. This calcite-mud mixed with clay and fine detrital minerals makes up the larger proportion of the rock.

The relatively unreactive greenish rock differs microscopically from the reactive rocks. There is much less calcite and more quartz and clay. The dolomite is present as crystals which are well formed, as in the reactive rocks.

Thin sections were prepared from reactive rocks which had been soaked in 2M NaOH. Under the microscope they appeared quite similar to untreated rock. Dolomite rhombs were still intact and qualitative study did not reveal that dedolomitization had occurred (2, 3). Micro-cracks were present in some sections.

Examination of polished surfaces of affected concrete showed thin dark rims surrounding some of the aggregate. Such rims were less apparent when thin sections were examined. In reacted concrete, cracks were visible which intersected both aggregate and cement paste.

The most significant features of the petrography of the reactive rocks are as follows:

1. There is a considerable amount of both dolomite and calcite in the carbonate fraction.
2. The dolomite crystals are well-formed rhombohedra often reaching sizes of about 0.05 mm across or larger. Other minerals in the rocks are commonly finer and below the limits of resolution of the optical microscope. This imparts a fine-grained texture to the rocks.
3. There are clay minerals distributed throughout the carbonates sometimes giving the rock a murky appearance to microscopic observation.
4. They often have a low porosity.

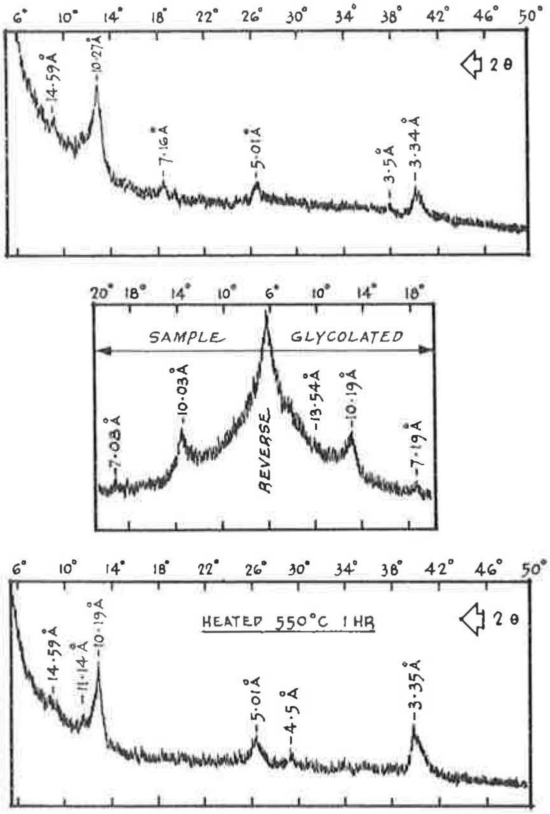
Mineralogy

The minerals of which the Kingston rocks are composed have been described in detail (13). Microscopic, X-ray diffraction, and differential thermal analyses were performed on concentrates and residues.

Separations.—Sufficient dolomite was concentrated from the reactive rocks for a partial chemical analysis and for analysis by powder X-ray diffraction. The mineral is less soluble in acid and has a higher specific gravity than calcite; it also occurs as larger crystals in the Kingston rock. These differences were exploited in the separation procedure adopted. Sink-float methods in heavy liquids, a Frantz isodynamic magnetic separator, and sedimentation techniques were all employed. As clay occurs as inclusions within the crystals it was not possible to obtain a completely pure concentrate of dolomite.

Small concentrates of other minerals separated at various stages in the separations were also examined.

The acid-insoluble fraction of the rock was also separated. During this work the possibility of dissolution by acid treatment of swelling clay minerals was considered. Some of these, notably hectorite, are known to be acid soluble. A technique in which solution of the carbonate was effected by ion exchange resin was adopted. This was an adaptation of a procedure described by Ray, Gault and Dodd (14). Investigation showed that it was possible to detect hectorite, added to the sample, in a concentration of only 1 percent. In later phases of the work, dilute acetic acid and dilute hydrochloric acid were used. Prior to analysis, the clay minerals were flocculated with $CaCl_2$ to replace hydrogen with calcium ions on the exchange sites.



SETTING OF GENERAL ELECTRIC CO. DIFFRACTOMETER
XRD-5

EXIT SLIT: 3°
SOLLER SLITS: MEDIUM RESOLUTION
RECEIVING SLIT: 0·2°
RESPONSE: LINEAR
FULL SCALE DEFLECTION: 200 C.P.S.

TIME CONSTANT: 2
X-RADIATION: Cr
FILTER: V
KV: 50
mA: 16
SCANNING RATE: 1°/MIN.

Figure 11. X-ray diffractometer patterns of acid-insoluble fraction of composite Kingston rock which had been soaked in 2M alkali for several months.

The Carbonates.—In ideal dolomite there are an equal number of calcium and magnesium ions per formula unit. It is known, however, that dolomite may incorporate other ions in the lattice and also that there may be an excess of calcium above the ideal 50 mol percent (15). Such dolomite is known as protodolomite and is metastable although it may persist for periods of time measurable on the geological scale. It may be detected by X-ray diffraction as there are characteristic effects on its powder pattern by which it may be distinguished from ideal dolomite.

Substitution of iron or manganese in place of magnesium may produce similar effects on the powder X-ray diffraction pattern to those produced by substitution of calcium for magnesium (15). The partial chemical analyses showed the dolomite concentrated from the Kingston rocks contained only about 1 percent iron and even smaller amounts of manganese. The quantities found were insufficient to account for the effects observed on the X-ray diffraction patterns. It was concluded that the dolomite in all the Kingston rocks examined was of the metastable type in which there is an excess of calcium ions incorporated in the lattice. A similar study of calcite in Kingston rocks showed that small amounts of ions such as magnesium with a smaller radius than calcium were held in solid solution in the mineral.

Clay Minerals.—The mineralogy of the clays in the acid-insoluble fraction of the Kingston rocks was investigated in detail. It was considered possible that swelling clay minerals were present in the rock or developed from non-swelling clays as a result of the action of alkali. For this reason the methods of separation which were found to be least destructive to clay minerals were employed, in case acid-soluble expansive clay minerals were present. No expanding lattice clay minerals were found, however, either in the original rock or in the rock which had been soaked in 2M NaOH. Clay minerals separated from rock which had been soaked in alkali were not detectably different from those in the untreated rock (Fig. 11). The clay minerals identified were illite with lesser amounts of chlorite. These identifications were made by X-ray diffraction and differential thermal methods of analysis. The illite was found also to be intergrown with variable amounts of organic material (13).

Residues.—Small concentrates of detrital minerals were obtained at various stages of the separations. Tourmaline, limonite, pyrite, and ceylonite were among minerals identified by microscopic methods. In some instances identification was confirmed by powder X-ray diffraction photographs.

An attempt was made to concentrate active silica, such as opal, which may have been present in the rock. This mineral has been held responsible for some of the worst cases of alkali-silica reaction (16), and although there was very little microscopic evidence for gel formation, its presence was suggested by adsorption studies (17). The acid-insoluble fraction of the reactive Kingston rocks was studied by the sink-float technique using a liquid of specific gravity 2.4. Very little material was light in this liquid and no active silica was detected in any sample.

Chemistry

Chemical analyses were obtained on the rocks as total solid and on the acid-insoluble fraction. Partial chemical analyses were also obtained on the dolomite concentrated from some of the rocks. The reactive rocks have an acid-insoluble content of 6 to 17 percent and the non-reactive greenish rock contains 40 to 45 percent acid insoluble. A computation was performed in which oxides were recombined into minerals. This supported the X-ray and petrographic finding that the rocks are of intermediate composition between limestone and dolomite. The analyses showed that the acid-insoluble fraction of the reactive rocks is quite similar to an "average shale" (18). Pyrite is known to occur in the rocks but computation showed that sulfur is likely to be combined with carbon as well as iron.

There was no apparent relationship between reactivity and oxide content or computed mineral composition.

Studies of Other Carbonate Rocks

It has been recognized for many years that rocks which are of intermediate composition between limestone and dolomite are less common than are the end members of the series (19). The reactive rocks fall within this relatively uncommon range of composition. This suggested that other rocks of this general composition might display similar reactivity to those from Kingston. It was decided to assemble a suite of carbonate rocks covering the composition range from limestone to dolomite. The dolomite was apparently the only mineral in the Kingston rock attacked by strong alkali. Insofar as possible the rocks obtained were low in acid-insoluble content. It was hoped by this means to verify the tentative conclusion that the acid-insoluble minerals played no part in causing expansion. At the time, this also seemed to be supported by the composition of the Kingston rocks, some of the most reactive of which had an acid-insoluble content of only about 5 percent.

During the autumn and winter of 1959-60 a suite of more than 50 rocks was assembled. The rocks covered the composition range from limestone to dolomite and were generally low in acid-insoluble minerals. Considerable difficulty was experienced in obtaining rocks in the intermediate range of composition which were also low in acid insoluble. Samples were only obtained through the cooperation of many individuals in public and private concerns in Canada, the United States and the United Kingdom. Additional samples, known to be reactive, were supplied to the authors from Virginia and Indiana by H. Newlon, D. Hadley, and W. L. Dolch.

The rocks were crushed and sized and used as aggregate for concrete beams. Each sample was used for two pairs of beams; one pair was made with high alkali cement and one pair with low alkali cement. These beams were conditioned in the fog room at 73 F and length change recorded. Rock prisms were also cut and immersed in 2M alkali. Length measurements were recorded at weekly intervals.

The rocks were analyzed for Ca, Mg, Fe and acid-insoluble content. More than 60 microscopic thin sections of these rocks and more than 100 thin sections of the concrete were prepared and examined. As anticipated, the rocks differ widely in petrographic character. Degree of recrystallization, size of crystals, distribution of dolomite, grain shape, and porosity all vary. The majority of the rocks, however, caused no abnormal expansion in the concrete beam or rock prism tests. None of the rocks with a very low acid-insoluble content caused expansion but considerable expansion was recorded from rock containing about 5 percent acid insoluble. Reactive rocks had in common the invariable presence of dolomite, calcite, and acid insoluble although the proportions varied. They also shared some or all of the petrographic features of the Kingston rocks, some of the most reactive being closely similar in composition and petrography to those from Kingston.

METHODS OF TEST AND IDENTIFICATION

ASTM Tentative Test Methods

This laboratory had previously concluded that the ASTM methods of test for cement-aggregate reaction failed to classify the reactive Kingston rock as excessively expansive in concrete (1, 2). In the mortar bar test (ASTM C227) the reactive Kingston limestone showed "more than the normal expansion with high alkali cements," but this expansion did not exceed the then accepted limits of 0.05 percent at 3 months and 0.10 percent at 6 months for alkali-reactive aggregates. Early uncertainties as to the nature of the reaction led this laboratory to carry out an extensive series of C227 tests, involving some 100 mortar bars. The main variables studied were (a) different reactive and non-reactive materials, (b) cement and cement-alkali contents, (c) water-cement ratios, (d) aggregate gradings, (e) possible inhibitors, and (f) period of test. None of the modifications attempted made this method more effective for this particular case. Necessary reduction of the expansive rock to sand size, as required by this test, reduced the extent of expansion considerably as compared with the expansion of concrete prisms made with the same rock as coarse aggregate (2).

From these studies, of which typical results have been published (1, 2), it was concluded that the mortar bar test could not be made applicable to the Kingston material unless a new set of lower limits were established to distinguish excessive from non-excessive expansion. When subsequent studies showed that the Kingston phenomenon was something different from the alkali-silica reaction, for which the ASTM tests had been developed, the "apparent weakness" of these tests became understandable. On the basis of the work done in this laboratory, the concrete prism test, discussed in a later section, is considered superior to the mortar bar test.

The quick chemical test (ASTM Method C289) did not reveal the reactive Kingston rock as deleterious. The inadequacy of this test for dolomitic limestones has been long recognized (20). When applied to the insoluble residue portion of the rock, the results were inconclusive, which is consistent with a non-siliceous reactivity (2).

The Conrow test (ASTM Method C342) also failed to show the deleterious expansion in the reactive Kingston rock. This could be expected as this test is highly specific for certain siliceous aggregates which are not necessarily alkali reactive. This laboratory carried out this test on more than 100 mortar bars made with various combinations of materials.

Expansion of Concrete Beams

The most reliable test for determining the expansive properties of reactive carbonate rock is the measurement of length change of concrete prisms (9). Direct comparison can be made between aggregates and between low and high alkali cements. Use can be made of standard laboratory facilities such as molds, inserts, comparator, and fog room. The one disadvantage is that several months may be required for cases of moderate to low reactivity. The test may be accelerated, however, by conditioning at 100 F and 100 percent R.H., rather than in a curing room. Comparison samples of non-expansive combinations are necessary in this test.

Establishing limits for the expansion that can be tolerated in field concrete would depend on the function of the concrete element in question. It is suggested that, for ordinary cases, a limit of 0.02 percent in 6 months be placed on prisms of 3 by 4 by 16 in. conditioned at 73 F and 100 percent R.H.

Laboratories having apparatus for the Scholer wetting-drying test can obtain very similar results to those obtained by this test (1, 2).

Expansion of Rock Prism

Measurement of length change of saw-cut rock prisms immersed in 1 to 2M solutions of alkali will produce expansions of alkali-reactive carbonate rock of the same order as for concrete prisms (2). Care must be taken to avoid cracks, joints, cleavages or other planes of weakness that may produce spurious results. This may be largely overcome by the use of smaller specimens as in a comparable test developed by the Portland Cement Association (3).

The time for this test to yield significant results is from two to six weeks, depending on size of specimen, concentration of alkali, and reactivity of aggregate. Comparison specimens of non-reactive carbonate rock are necessary.

Powder-Cell Test

The procedure and apparatus are referred to in an earlier section, and in greater detail elsewhere (12). The powdered rock is treated with alkali in a compression chamber fitted with a rubber membrane. Expansion in the powder is measured by liquid in a capillary tube.

This method has an advantage over the rock prism test in that samples can be made more representative, variations due to directional properties are eliminated, and the fine particle size gives a rapid response. The length of time to complete a test is about one month. Parallel runs with non-reactive rock are necessary for comparison.

Petrographic and Other Criteria

It is not possible to say with certainty by petrographic criteria whether a particular rock will cause excessive expansion if used as aggregate with high alkali cement. Aggregates so far known which cause trouble are, however, apparently restricted as to rock type. The criteria for recognition have been discussed in a previous section and in earlier publications (3, 13). Although there is no direct relation between chemical composition and reactivity, some degree of elimination of non-reactive rock is possible by analysis. The rocks which expand excessively contain both calcite and dolomite ranging from about 40 to about 60 percent of dolomite, and an acid-insoluble content ranging from about 5 to about 20 percent. They are invariably fine grained, and generally of relatively low porosity or absorpition.

Exceptions to these composition criteria have been observed. It is possible that some of the apparent discrepancies may be due to analytical factors. The quantitative determination of magnesia by chemical methods is subject to considerable variability in results depending on the nature of the parent material and on the methods used. Such differences may be further magnified when the magnesia values are converted into percent dolomite. Determination of acid-insoluble residue is even more subject to variability as a study of the method would show.

Identification of the expansive type of alkali-carbonate reaction in affected concrete by petrographic examination is also far from certain. It is not established that rim formation on aggregate particles is a necessary consequence of the reaction. The occurrence of fracturing in the mortar and aggregate can result from other causes. The only known end product of the reaction is brucite; however, this may also be present in non-expansive dolomitic rock.

SOME POSSIBLE MECHANISM OF EXPANSION

At present there is what may almost be described as a plethora of suggested mechanisms which have been proposed to account for the expansion in alkali of reactive carbonate rocks. This results from the lack of conclusive experimental evidence in support of any one hypothesis.

The extensive tests on the suite of carbonate rocks ranging in composition from limestone to dolomite and of varying petrography showed that expansive reactivity is rather uncommon. It is also not likely to be a coincidence that many of the expansive rocks from different areas resemble one another petrographically. In particular these rocks contain well-formed dolomite euhedra which are of fairly even distribution in the rock. The groundmass consists largely of fine-grained calcite which is in the micron size range and often has a dusky brown appearance in thin section. There is an acid-insoluble content of not less than 5 percent.

Mineralogical studies showed that the clay minerals were of the non-swelling type. The simple hypothesis that expansion was due to the presence or formation of swelling clay minerals had therefore to be abandoned.

An interesting approach is provided by the work of A. A. deGast (Department of Mining Engineering 1962, Queen's University, M.S. thesis, unpublished). He postulated that expansion of the rock resulted from release of residual elastic strain due to the removal of restraint. The stored energy was inherited from earlier epochs and resulted from geological processes acting on the calcite and dolomite which have different rheological properties. In support of this, reference is made to work by Handin (21) and Griggs (22). Handin showed that dolomite is ten times more resistant to deformation than calcite and Griggs demonstrated that, unlike calcite, dolomite is not susceptible to recrystallization. It is concluded that elastic strain, if present, is stored in the composite grains of the material. The supposition of stored elastic energy within the rocks of the Kingston area is supported by several field examples.

A laboratory investigation was made in which strain was measured by the photoelastic technique. This is of high sensitivity and permits the detection of intergranular strain. Measurements were made on limestone wafers and cubes and an evaluation was made of the strain distribution in concrete.

It was shown that shear strains were present around aggregate of defective concrete. Studies of the limestone prisms confirmed the results obtained by other workers that the alkaline solution is the major factor contributing to deterioration. Expansion due to elastic readjustment of inherent elastic energy was concluded to be of minor importance.

There is additional evidence to show that release of residual elastic strain is not the underlying cause for expansion of the Kingston rock in alkali. In particular, little or no residual intergranular strain is likely to remain in rock which has been powdered to a crystallite size of the same order as the component minerals. Large expansions have, however, been registered by Kingston material in the powder-cell test. There is also evidence to show that the clay fraction is involved in the expansive mechanism. It is very unlikely that clay minerals would play a special role in retaining elastic energy in the manner postulated.

The dedolomitization reaction (2, 3) is the only significant chemical change known which takes place when these rocks are placed in an alkaline environment. Dolomite is attacked by the alkali hydroxide with formation of alkali carbonate, calcium carbonate (calcite), and magnesium hydroxide (brucite) (Fig. 12). The reaction was considered at an early stage as the underlying cause for expansion. Calculations of the unit cell sizes, however, showed that the combined volume of the known solid products was less than the initial volume of the dolomite. The lattice parameters of the brucite and calcite formed in the reaction also appear normal.

Solubility data suggest that the Na_2CO_3 formed in the reaction should pass into solution. There are hydrated double salts of large cell volume such as gaylussite ($Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$) and pirssonite ($Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$). When a mixture of calcite and dolomite was covered with 2M NaOH and left to evaporate slowly for several weeks, X-ray examination of the product showed portlandite and pirssonite to be the dominant phases, together with brucite and calcite.

The rock-alkali mixture forms a multi-component system the phase relations of which have not been worked out. The system sodium carbonate-calcium carbonate-water (Fig. 13), however, although less complex, includes some of the most important components in the rock-alkali system. Therefore, phases in the rock-alkali system are likely to develop only at quite similar temperatures and concentrations to those shown in Figure 13. In particular it is very probable that at 22 C a considerable concentration of Na_2CO_3 in solution will be required for the crystallization of gaylussite. The inevitable conclusion, based on any sensible assumption as to concentration, is that neither hydrates nor hydrated double salts are likely to form in the rock when it is immersed in 1 or 2M NaOH.

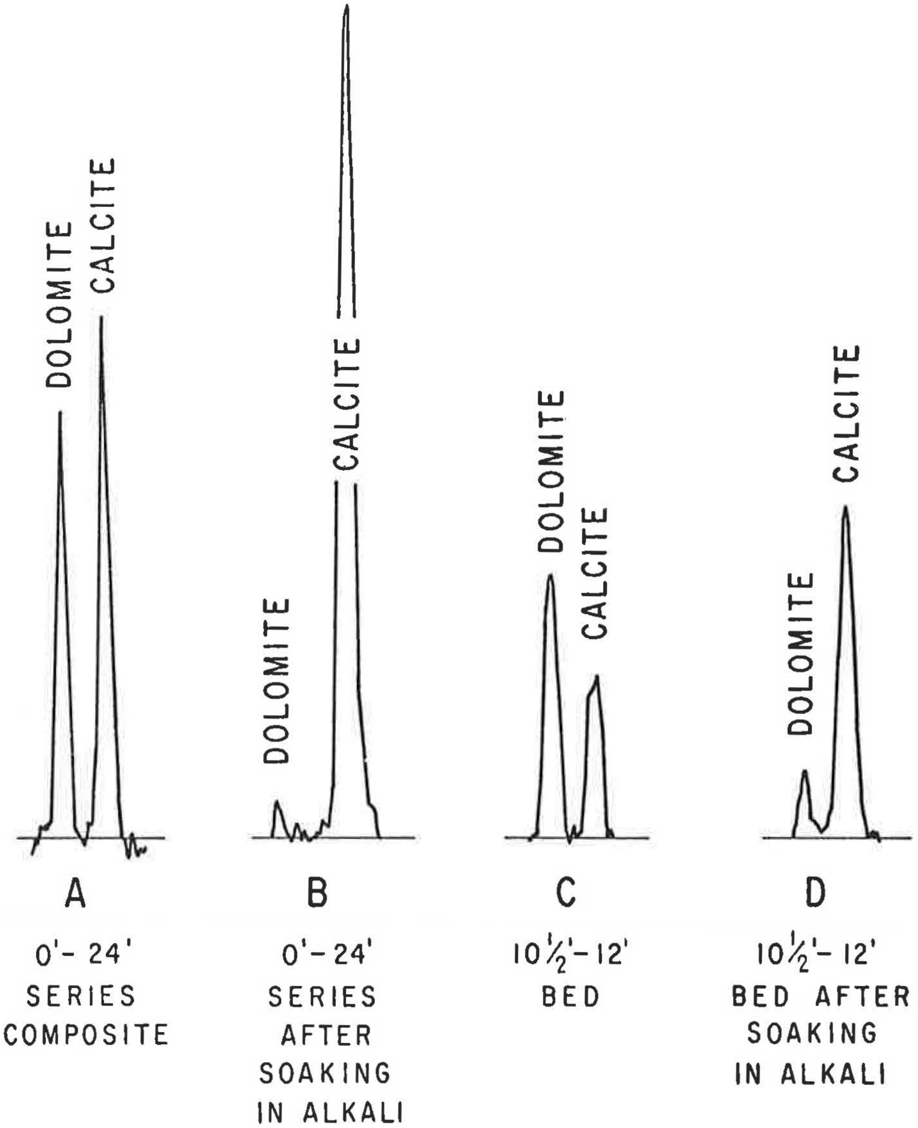


Figure 12. Dedolomitization on treatment with alkali.

Also there is no evidence from X-ray diffraction studies for the crystallization of minerals of this sort in the reactive rock which expanded under conditions that prevented evaporation of alkali.

Differential thermal studies of unwashed alkali-treated powders gave complex curves. Although there was some correspondence to thermograms of gaylussite, the evidence was far from convincing because alkali-treated powders which failed to produce expansion in the powder-cell test also gave thermograms which were closely similar to those from the reactive rock (Fig. 14). The situation is also complicated by the presence of Na_2CO_3 and possibly by hydrates formed on drying the material after its removal from the alkali.

It was concluded that expansion did not result from formation of hydrated double salts or alkali-carbonate hydrate for the following reasons:

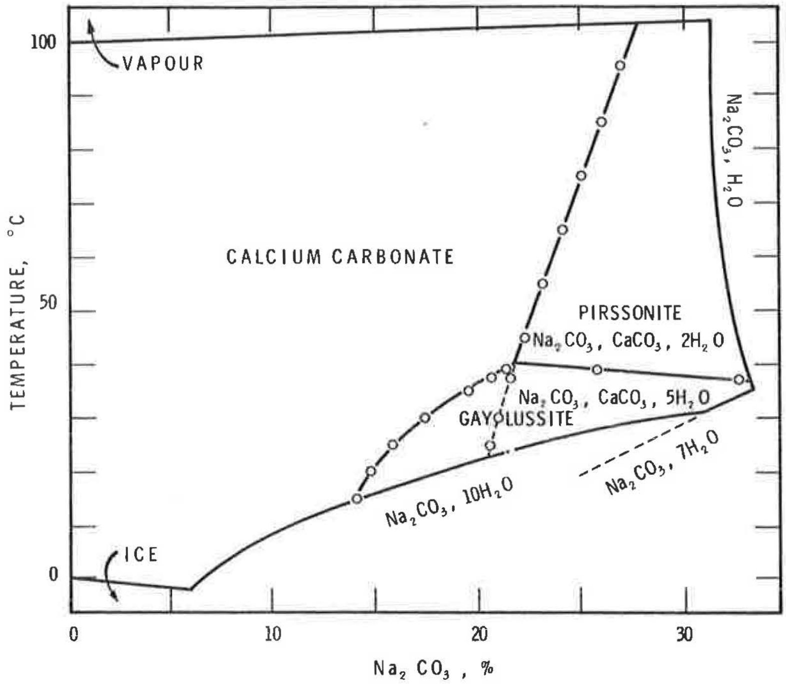


Figure 13. The system sodium carbonate-calcium carbonate-water (after Bury and Redd (23)).

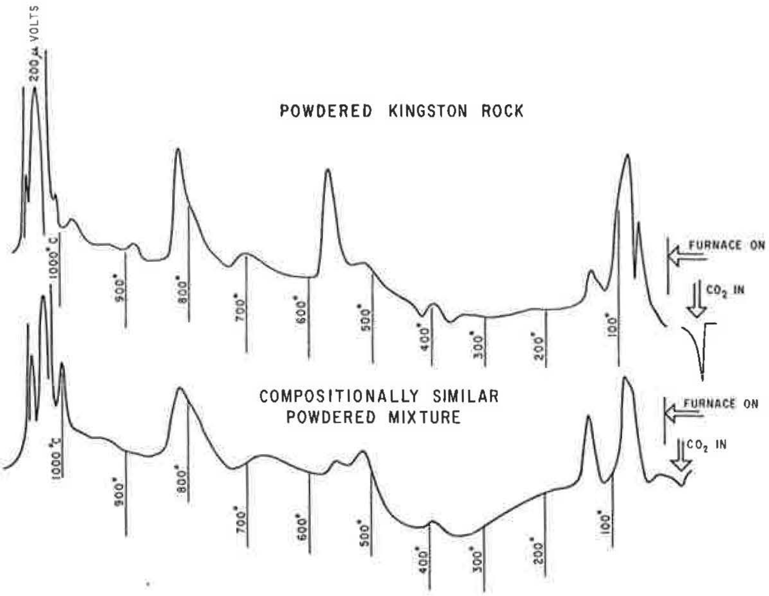


Figure 14. Thermograms of expansive Kingston rock and compositionally similar, non-expansive mixture after treatment in 2M NaOH for 14 days. Samples dried in air for 1 hour.

1. Expansion begins quite soon after the reactive rock is placed in 2M alkali when the concentration of alkali carbonate is very low.
2. Alkali carbonate formed, due to dedolomitization, is highly soluble and is unlikely to form a solid phase in a 2M solution of alkali.
3. Phase data suggest that the concentration of alkali carbonate is much too low for gaylussite or alkali-carbonate hydrate to form (Fig. 13).
4. Calculations made in this laboratory show that a concentration of gaylussite in excess of 1 percent would be required to account for the observed expansion.
5. An addition of 1 percent gaylussite was detectable by X-ray diffraction.
6. No hydrated double salt was detected by X-ray diffraction analysis unless the concentration of solution was allowed to rise by evaporation.
7. Concrete beams held at a relative humidity of 50 percent or lower for more than 2 months showed no expansion (Fig. 4). Under such conditions the concentration of alkali salts would be expected to be at a maximum. These beams expanded rapidly as soon as moisture was made available.
8. Powdered mixtures of the same composition as reactive rock showed neither expansion nor water imbibition when tested in the powder cell even though dedolomitization occurred.

The crystallities of which the matrix is composed are quite similar to those in lithographic limestone. The very fine crystallite size is likely to result in high chemical reactivity which it seemed possible was connected with the expansion. Samples of Solenhofen lithographic stone (obtained from Wards Mineral Suppliers) showed no reactivity. For this and other reasons it is most likely that the significant textural property is the distribution of the clay minerals.

It was proposed by Feldman and Sereda (17) that material with gel-like properties formed in the rock as a result of the alkaline attack. Water imbibition is a property of some gels. Materials develop these properties when in the colloidal size range. The suggestion was therefore made that the products of dedolomitization were trapped within the rocks' very fine pore system as crystals of colloidal sizes. This was not confirmed by an investigation of the half-peak breadths of the X-ray powder lines of the brucite and calcite (24). The treated rock, however, does show an increased surface area and especially an increased capacity for holding water after saturation (17). If these characteristics are not due to the products of the dedolomitization reaction then they must be due to the parent material, such as the clay fraction, which becomes uncovered by the reaction. The dolomite euhedra contain inclusions which are apparently of clay (Fig. 10), and such crystals of clay will become exposed as a result of the dedolomitization reaction. Cracks and channels will open up and allow access of alkali to clay in the matrix. It is postulated that such clay is in an "active" state quite different from that found after extraction with acid and flocculation with $CaCl_2$. It is this "active" clay, released during dedolomitization, which contributes to the expansion. The steps in the hypothesis now proposed are (a) dedolomitization exposes "active" clay minerals; (b) exchange sites on the clay surface adsorb some sodium ions; and (c) water uptake by this "new" clay results in swelling.

This hypothesis with evidence based on the powder-cell test is described in detail in another papaer (24).

It is not thought that the ability to expand is the sole prerogative of rocks which resemble those from Kingston or that deleterious expansion will necessarily be caused by such rocks. The fact that rocks of this type from several different and widely separated localities do cause excessive expansion in concrete made with high alkali cement indicates, however, that such rock should be regarded with suspicion as potential aggregate. Rock of this type can be readily recognized by petrographic examination and should be subjected to careful tests, such as the concrete beam test, prior to use as aggregate with high alkali cement.

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Studies on the Mechanisms of Alkali-Carbonate Reaction

Part I. Chemical Reactions

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•AN understanding of the mechanisms of alkali-carbonate rock reaction which result in expansion of concrete is of primary importance in dealing with the resultant problems on a practical level. This paper reports results of laboratory studies made to determine the contributory chemical reactions that may take place. Results of parallel studies on such physical aspects as internal structure of and access of alkalies into various carbonate rock types are not included, but will be published at a later date.

The method of approach has been to consider each of the three major minerals or groups of minerals that normally make up carbonate rocks; i.e., quartz, clays and carbonates. These were investigated through studies of pure minerals, as well as reactive and non-reactive rocks, to determine what possible role each might play in observed expansion in the composite system.

These major constituents were analyzed and measured by a variety of methods to determine chemical composition, phase composition, and volume and mass of the materials before and after exposure to sodium and potassium hydroxide solutions. (Mass and weight are used interchangeably throughout this paper.) Evidences of reactions noted during this portion of the study were then sought in thin sections, test prisms, and in aggregate from laboratory and field concrete.

MINERALS AND ROCKS UTILIZED

The calcite and dolomite minerals used in this study were high-purity coarsely crystalline materials. The dolomite was the snow-white variety obtained from Wards Natural Science Establishment, Inc., and was shown by chemical analysis to contain 46.4 percent $MgCO_3$. The calcite was a clear-to-white vein material containing less than 1 percent $MgCO_3$ and was collected at Harrisonburg, Virginia.

Approximately 300 hand samples and data on their composition and expansivity as measured by the prism test described by Hadley (6) were available for this study from a previously conducted statewide survey for reactive carbonate aggregates from Virginia commercial aggregate sources (Newlon and Sherwood, 10). These rocks included a great variety of lithologic types exhibiting wide ranges in composition, texture and reactivity. Samples exhibiting extremes in composition and expansion as well as more representative rock materials were utilized from this suite.

EFFECT OF ALKALIES ON QUARTZ AND CLAY

Quartz

In all the rocks studied, quartz was present in quantities easily detected by thin section or X-ray analysis. The actual percent of quartz varied from about 1 to as high as 40. Petrographic studies indicated this material to be dominantly a dense, well-

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TABLE 1

ROCKS SELECTED FOR QUARTZ AND CLAY MINERAL STUDIES

Rock[1]	Ratio: Dolomite/Total Carbonate	Quartz (%)	Clay (%)	Prism Expansion, % (8 weeks)
1-8	0.63	9.5	16.3	0.69
5-1	0.18	6.5	13.1	0.13
26-5	1.00	1.0	4.8	0.02
35-6	0.09	8.0	1.0	0.01
22-2	0.80	2.0	18.5	-0.01
32-2	0.56	1.0	18.5	-0.02
1-17	0.03	2.0	1.0	-0.08

[1] The two-number designation of the rock samples has been carried over from the previous work (9). The first number designates the quarry, the second the sample taken from that quarry.

crystallized, clear quartz with only minor amounts of chert. However, a considerable amount of clay-sized quartz with a high surface area to volume ratio was present in all the samples and the susceptibility of this material to attack by strong alkalies might be suspected. To investigate this possibility, two chips for thin sectioning and 3 gm of -200 mesh material were prepared from each of several rocks showing a large variation in composition and reactivity (Table 1). One chip was soaked in 1N NaOH for three months, and one-half of the powdered rock was soaked for four weeks. (The effects of NaOH have received most attention in these studies because induced expansions of reactive rocks were previously determined to be greater with NaOH than with KOH (6, 9).) Subsequent to the alkali exposure, thin sections were made from both the soaked and unsoaked chips, and the rock powders were analyzed by X-ray diffraction. In each case, no significant change could be discerned in the amount or nature of the quartz present. The clay-sized fractions of the insoluble residue of these rocks were also exposed to strong alkali solutions and X-rayed for quartz with similar results.

These test results, together with lack of visible evidence (gel, etc.) of alkali-silica reaction in laboratory and field concrete, have led the authors to disregard quartz as a deleterious constituent in any of the carbonate rocks studied to date.

Clays

Clay minerals, like quartz, were present in every carbonate rock analyzed during this study. The amount of clay is often difficult to measure accurately because of problems encountered in separating the fine quartz particles from the clay fraction. Several X-ray methods have been suggested (1, 5), and the authors are now experimenting with modifications of these. Generally, X-ray diffraction methods using an internal standard for determining quartz in the insoluble residue of a carbonate rock and designating the remainder of the residue as clay, providing no other minerals are present in large amounts, have been found to be satisfactory for most of the work done to date. These techniques indicate that clay contents of more than 15 percent are not unusual in the Virginia carbonates.

To investigate the effects of strong alkali on the clay fraction of the carbonate rocks the seven samples given in Table 1, which represent both reactive and non-reactive rocks and also wide variations in the carbonate minerals and insoluble residue contents, were utilized. Each rock was ground to -50 mesh and treated with a 0.23N HCl, which was added in small increments until vigorous reaction ceased. This concentration was previously determined to have essentially no effect on the clay minerals present.

The clay fraction was separated, dried and identified by X-ray diffraction. The clay species found in both reactive and non-reactive rock from the Virginia portion of the Appalachian geosyncline are very similar, consisting almost entirely of a 10Å illite and a 14Å chlorite. This chlorite varies slightly from sample to sample but appears to be a magnesian variety.

Clay fractions of rocks 1-8, 5-1 and 1-17 which showed high, moderate, and no alkali reactivity, respectively, were each split into three parts. One-third was put into 1N NaOH and another in 1N KOH for a period of one year. The remaining one-third was kept sealed and dry as a standard. At the end of one year, all three parts were oriented by settling on glass slides and studied by X-ray diffraction. The only alteration evident in the X-ray diffraction patterns of the soaked versus unsoaked material involved the peaks representing d-spacings at approximately 7.68Å and 7.13A. The 7.68Å spacing seemed to have weakened during soaking, whereas the 7.13Å spacing appeared to have been reinforced. This phenomenon occurred with both NaOH and KOH exposures and was clearly evident in the clays from each rock type.

This alteration may be due to poorly crystallized chlorite (002 plane) being transformed to a better crystallized material during the soaking period. Heat treatment is reported to have this effect on some chlorites (3). The values of 7.1Å for this d-spacing is that generally evident in well-crystallized chlorites. In any case this minor alteration in crystal structure was observed to take place in both reactive and non-reactive rock and is of academic rather than practical significance in the present work.

EFFECTS OF ALKALIES ON POWDERED CARBONATE MINERALS AND ROCKS

Volume and Mass Changes

Based on the work of Swenson and Gillott (12), Hadley (6), and others, the breakdown of dolomite had been suspected as the major cause of the expansive alkali-carbonate reaction prior to the present work. The remainder of this paper is devoted primarily to data and observations taken from experiments investigating the effects of sodium and potassium hydroxides on calcite and dolomite mixtures and on carbonate rocks.

Mineral Calcite and Dolomite.—Experiments were designed to measure possible volume and mass changes in finely ground dolomite and calcite minerals exposed to alkali solutions. The first of these involved five discrete mixtures ranging from pure dolomite to pure calcite computed on a mole rather than a weight basis. Each of these mixtures was exposed to NaOH solutions with the following hydroxide to carbonate ratios:

$$\frac{\text{Equivalents of OH}^-}{\text{Equivalents of CO}_3^=} = 0,\ 0.25,\ 0.50,\ 0.75,\ \text{and}\ 1.00^1$$

All the mixtures were stored at 25 C in graduated cylinders and were stirred periodically for 22 weeks. At the end of this period the solid material was allowed to settle for several days to a constant level and its apparent volume was measured. Figure 1 shows the level of the solid materials after exposure to distilled water and to concentrated NaOH for 22 weeks.

Figure 2 shows the curves obtained by plotting apparent volume increase of solid material in the cylinders versus concentration of NaOH for several mixtures of calcite

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[1] Yielding NaOH concentrations of approximately 0, 1N, 2N, 3N and 4N, respectively, since the moles of carbonate and the volume of solution were kept constant. This rather unorthodox notation has been utilized in the present work because a primary concern was to determine how far these reactions would proceed toward completion in systems where not only concentration of solution but also the ratios of hydroxide to carbonate were known.

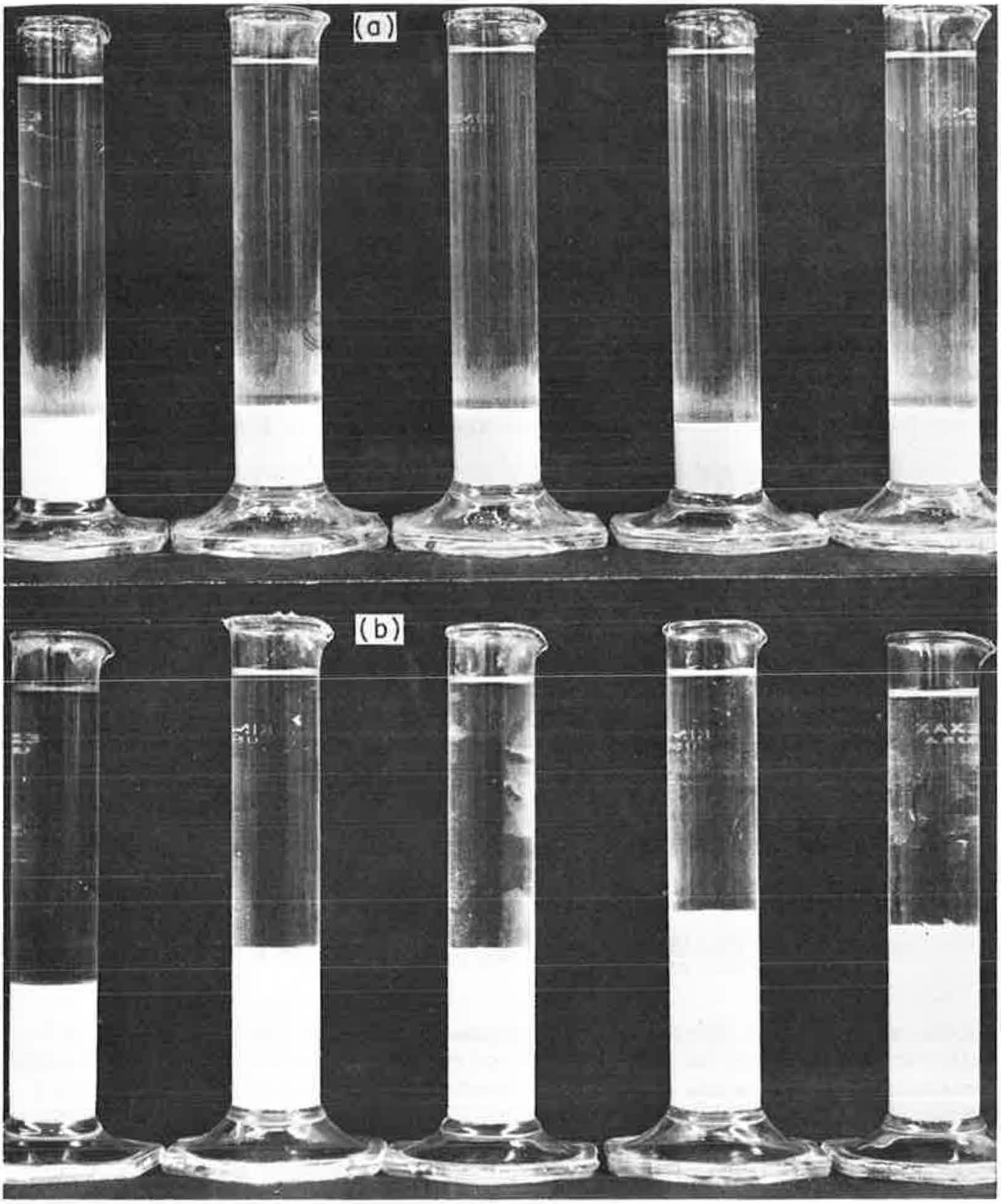

Figure 1. Mineral powders soaked for 28 weeks. Cylinders from left to right contain dolomite/total carbonate ratios of 0.00, 0.25, 0.50, 0.75, and 1.00: (a) effect of distilled water, and (b) effect of concentrated (Eq. OH^-/Eq. $CO_3^=$ = 1.00) NaOH solution.

and dolomite after twenty-two weeks. The data plotted in Figure 2 clearly show that: (a) mixtures ranging from all calcite to all dolomite exhibited significant apparent volume increases if the Eq. OH^-/Eq. $CO_3^=$ ratio was 0.50 or greater, and (b) volume change increased with increased dolomite content if NaOH was in the system. Parallel experiments showed no volume increase with time where dolomite powders were stored in distilled water.

The apparent volume increase of pure calcite is felt to be of particular interest, and the reactions which are thought to cause this are discussed in a subsequent section.

The second experiment was performed with KOH being used instead of NaOH. Again an apparent volume increase was observed. However two differences between the KOH and the NaOH soaks were noted. First, the observed increase in volume was nearly equal for a given concentration of KOH regardless of what mixture of calcite and dolomite was involved. Second, equilibrium in the system was very difficult to attain and probably was not reached in these mixtures. The experiments involving KOH were carried out several times over a period of months with stable temperature and frequent agitation, but the observed was about 25 percent for Eq. OH^-/Eq. $CO_3^=$ ratio of 1.0, and 15 percent for Eq. OH^-/Eq. $CO_3^=$ ratio of 0.5.

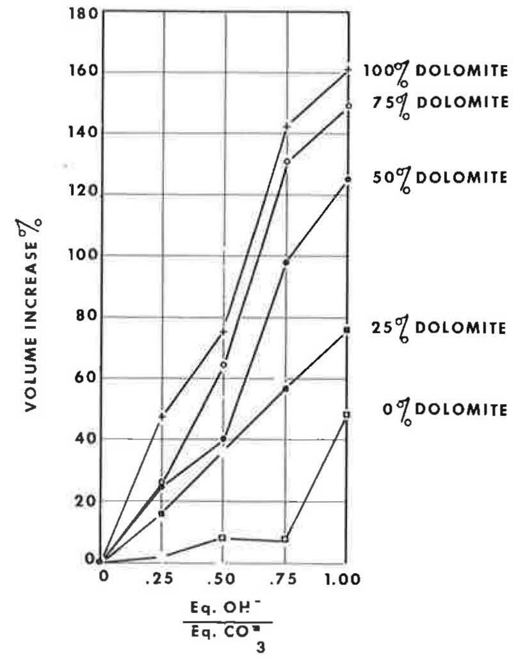

Figure 2. Volume increase vs concentration of NaOH at 22 weeks.

After volume measurements were completed for both the NaOH and KOH experiments, the mixtures were filtered, dried at normal temperature in a desiccator, and weighed. In general, the weight increases measured for the solid phases were similar to the apparent increases in volume. Table 2 gives the weight change measurements for 1.00 and 0.50 alkali to carbonate ratios of both the NaOH and KOH mixtures. Equilibrium conditions were probably not attained in every case, particularly in the KOH mixtures.

Rocks.—To substantiate the trends noted in NaOH soaks of the pure calcite and dolomite minerals, similar studies were made of carbonate rocks of widely different characteristics. Rock 1-8 is a highly expansive material with a relatively high insoluble residue content of 26 percent and near equal amounts of calcite and dolomite in the carbonate fraction. Rock 37-6 contracts slightly on prolonged exposure to NaOH. It contains a very low insoluble residue content of 1 percent and the carbonate is essentially all dolomite.

Five samples each of rocks 1-8 and 37-6, all containing equal moles of carbonate ion, were crushed to pass a number 200 standard sieve. Each sample was transferred to a graduated cylinder so that five cylinders were prepared for each rock, and equal amounts of carbonate ion were in all ten cylinders. NaOH solution was added to each rock, as in the mineral series, in increments of Eq. OH^-/Eq. $CO_3^=$ = 0.00, 0.25, 0.50, 0.75, and 1.00. The variation in the levels of the solid material at eight weeks is shown in Figure 3 for both rock types. Volume change versus time is shown in Figure 4.

Two points of possible significance are brought out by Figure 4: First, in rock powders with high surface area to mass ratios, volume increase is related directly to dolomite content regardless of the expansive tendencies exhibited by the original rock; and second, eventually expansion ceases with time and the curve levels off. The time required for completion of the expansive reaction is, of course, a function of grain

TABLE 2

WEIGHT CHANGE MEASUREMENTS OF FILTERED AND DRIED SOLIDS FROM REACTED ALKALI-CARBONATE MIXTURES

NaOH			KOH			Distilled Water		
Mole Ratio: Dolomite/Total Carbonate	$\frac{Eq.\ OH^-}{Eq.\ CO_3^=}$	Δ Weight Increase (%)	Mole Ratio: Dolomite/Total Carbonate	$\frac{Eq.\ OH^-}{Eq.\ CO_3^=}$	Δ Weight Increase (%)	Mole Ratio: Dolomite/Total Carbonate	Hydroxide	Δ Weight Increase (%)
0.00	1.00	40.2	0.00	1.00	31.6	0.00	0.00	-2.2
0.25	1.00	73.0	0.25	1.00	43.2	0.25	0.00	-1.7
0.50	1.00	94.8	0.50	1.00	31.4	0.50	0.00	-1.5
0.75	1.00	106.0	0.75	1.00	28.9	0.75	0.00	-1.9
1.00	1.00	120.0	1.00	1.00	29.9	1.00	0.00	-2.7
0.00	0.50	13.0	0.00	0.50	17.4			
0.25	0.50	28.8	0.25	0.50	19.6			
0.50	0.50	22.1	0.50	0.50	16.6			
0.75	0.50	26.7	0.75	0.50	20.4			
1.00	0.50	30.5	1.00	0.50	17.6			

size and agitation and not necessarily that shown in Figure 4. The expansion of the two rock powders ceased at the same time regardless of the percentage of dolomite present.

Figure 5 presents the data on volume change versus hydroxide concentration for the same rocks (1-8 and 37-6) at eight weeks. Concentrations of NaOH in excess of 0.50 did not result in increased volume change of the powdered 1-8. This is a probable result of all the dolomite reacting with NaOH and essentially no further expansive reaction taking place.

Identification of Reaction Products

After 22 weeks of exposure, the solid materials in each of the mineral NaOH soaks were filtered and dried, and selected ones were identified and semi-quantitatively analyzed by X-ray diffraction. The major finding of this X-ray work was the presence of considerable amounts of the hitherto unreported hydrated carbonate $CaNa_2(CO_3)_2 \cdot 5H_2O$, which is identical to the mineral gaylussite (see Table 3).

Figure 6 shows the X-ray diffractograms made of the dolomite mineral soaked in NaOH solutions of various concentrations. The sudden appearance and dominance of the gaylussite phase at high NaOH concentrations is graphically evident.

Table 3 shows that the gaylussite phase forms in considerable amounts when dolomite is exposed to high concentrations of NaOH. The reaction is less energetic, but clearly evident, when calcite is exposed in a similar manner. Intermediate mineral mixtures, as would be expected, show a progressive increase of the gaylussite phase with increased dolomite.

An interesting phenomenon brought out in Table 3 is the absence of calcite in the solid phase after equal equivalents of NaOH and dolomite have reacted. Sizable amounts of calcite remain when equal mole ratios of calcite and NaOH (lower right corner, Table 3) are reacted. The data indicate that the $CaCO_3$

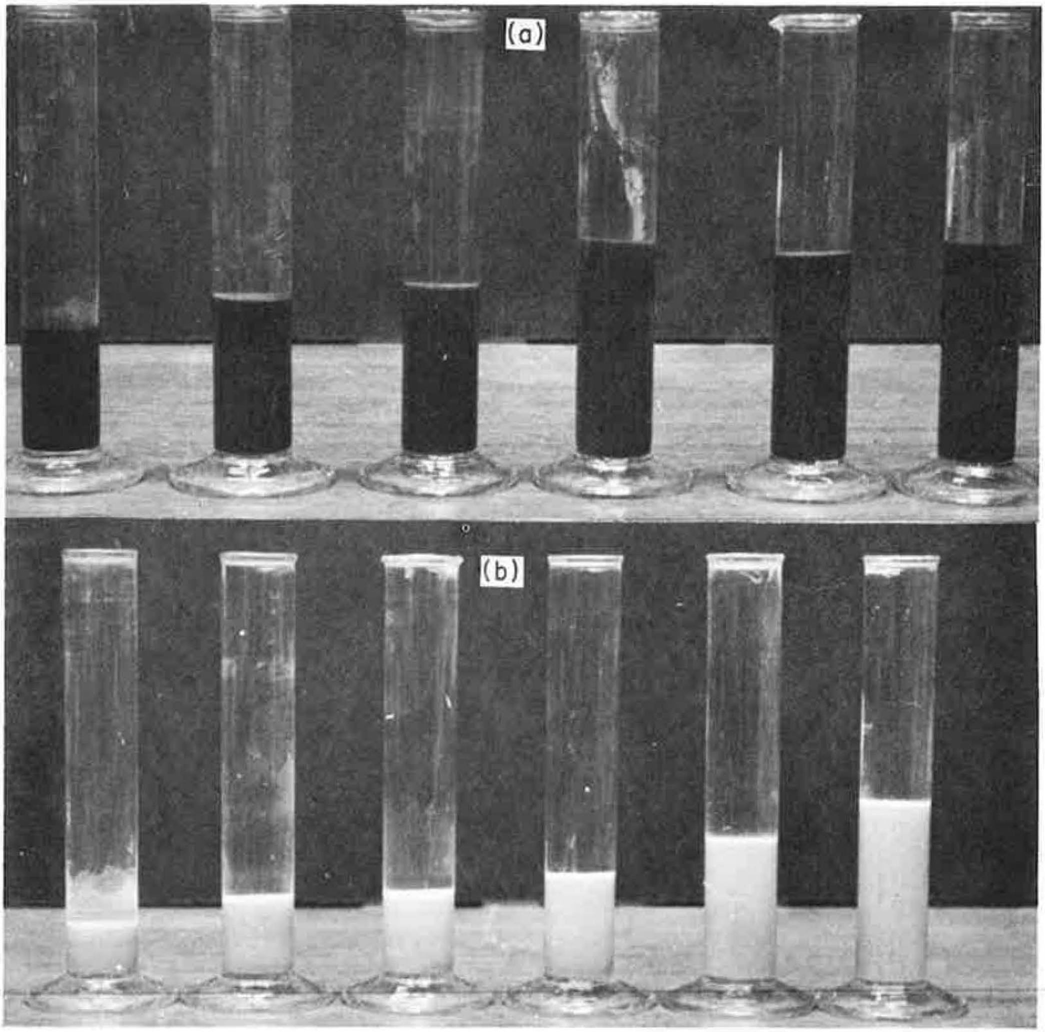

Figure 3. Rock powders soaked for 8 weeks. All cylinders contain equal moles of carbonate. Each set of cylinders contains NaOH solutions of the following concentrations (from left to right): Eq. of OH^-/Eq. of $CO_3^=$ = 0.00, 0.25, 0.50, 0.75 and 1.00: (a) contains aggregate 1-8, and (b) contains aggregate 37-6.

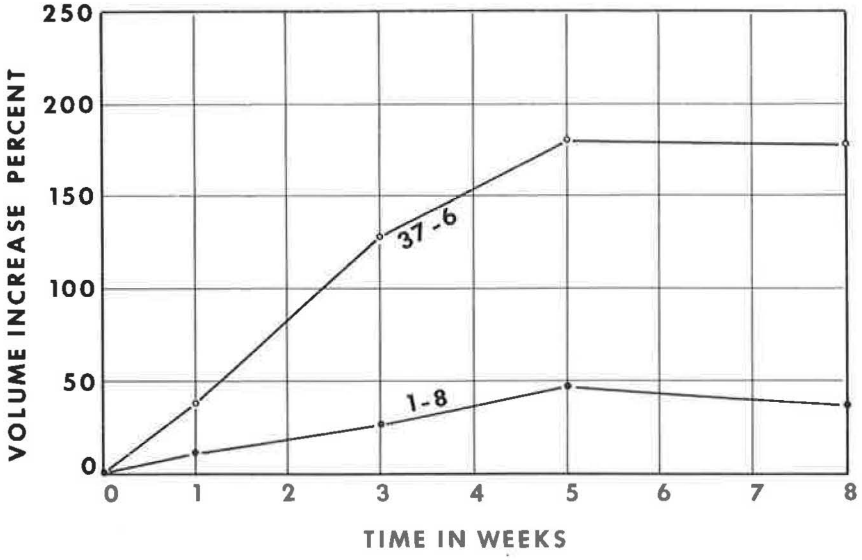

Figure 4. Volume change of powdered rock vs time. NaOH concentration Eq. OH^-/Eq. $CO_3^=$ equals one.

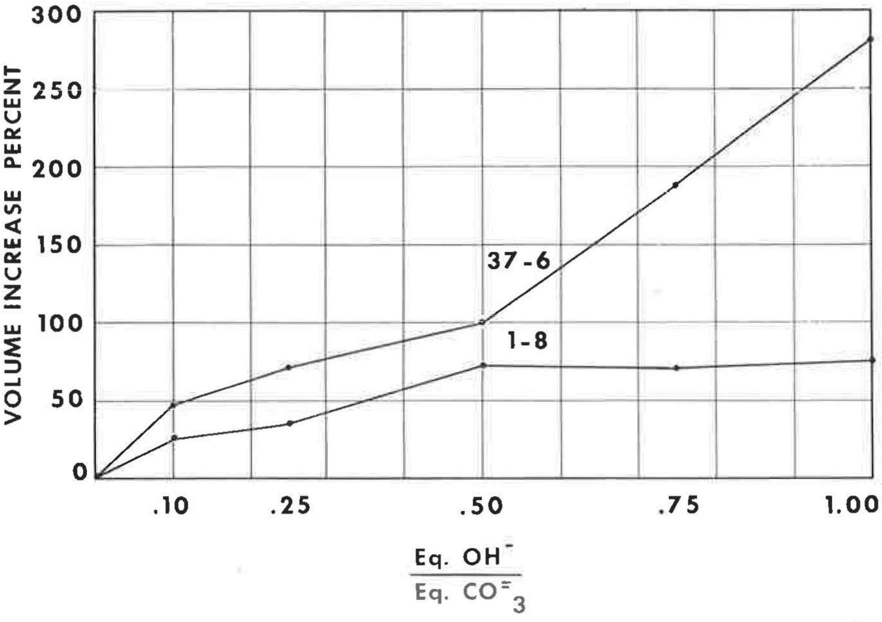

Figure 5. Volume change of powdered rock vs hydroxide to carbonate ratio at 8 weeks.

resulting from the breakdown of dolomite is considerable more reactive than the mineral calcite when exposed to NaOH solutions of equal normality.

Table 4 shows the phases present in KOH-carbonate mixtures. As in the case of NaOH the hydrated double salt, in this case, $Ca_2K_6(CO_3)_5 \cdot 6H_2O$, appears at high hydroxide concentrations. Other similarities to the NaOH reactants in Table 3 are (a) the

TABLE 3

PHASES PRESENT IN CARBONATE MINERAL—NaOH REACTANTS

Dolomite and Calcite (%)	NaOH $\left(\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}\right)$			
	0.25	0.50	0.75	1.00
Dolomite, 100	Calcite—moderate Dolomite—dominant Brucite—weak Gaylussite—not discernible	Calcite—moderate Dolomite—strong Brucite—weak Gaylussite—trace	Calcite—trace Dolomite—moderate Brucite—weak Gaylussite—dominant	Calcite—not discernible Dolomite—trace Brucite—moderate Gaylussite—dominant
Dolomite, 75 Calcite, 25	Calcite—strong Dolomite—strong Brucite—weak Gaylussite—not discernible	Not X-rayed	Not X-rayed	Calcite—weak Dolomite—trace Brucite—weak Gaylussite—strong
Dolomite, 50 Calcite, 50	Calcite—strong Dolomite—moderate Brucite—weak Gaylussite—not discernible	Calcite—dominant Dolomite—weak Brucite—weak Gaylussite—trace	Calcite—strong Dolomite—trace Brucite—weak Gaylussite—strong	Calcite—moderate Dolomite—trace Brucite—weak Gaylussite—strong
Dolomite, 25 Calcite, 75	Calcite—dominant Dolomite—trace Brucite—weak Gaylussite—not discernible	Not X-rayed	Not X-rayed	Calcite—strong Dolomite—trace Brucite—trace Gaylussite—strong
Calcite, 100	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—trace	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—trace	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—weak	Calcite—strong Dolomite—not discernible Brucite—not discernible Gaylussite—weak

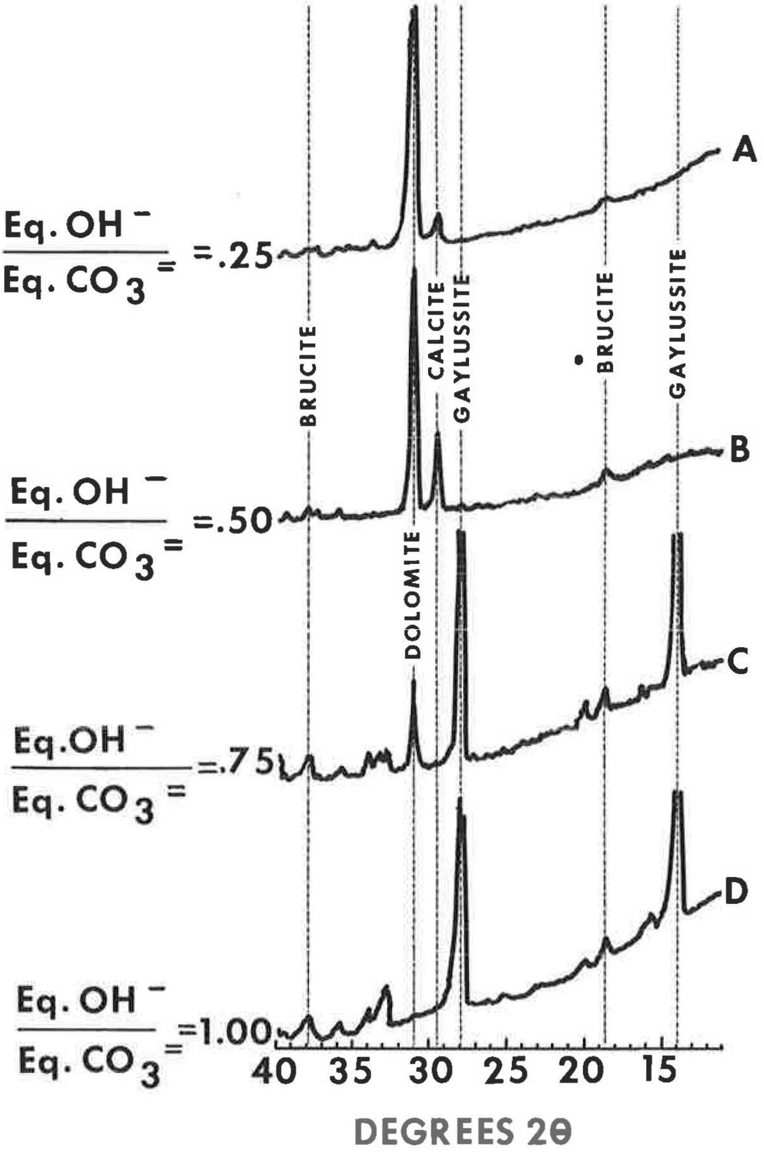

Figure 6. X-ray diffractometer tracings of mineral dolomite powders exposed to NaOH of different concentrations for 22 weeks. Diffractometer strips A, B, C and D were made from dolomite exposed to NaOH of Eq. OH^-/Eq. $CO_3^=$ = 0.25, 0.50, 0.75 and 1.00, respectively.

TABLE 4

PHASES PRESENT IN CARBONATE MINERAL-KOH REACTANTS

Dolomite and Calcite (%)	KOH $\left(\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}\right)$	
	0.50	1.00
Dolomite, 100	Calcite—strong Dolomite—very strong Brucite—moderate Portlandite—not discernible Buetschliite—not discernible	Calcite—not discernible Dolomite—very strong Brucite—moderate Portlandite—weak Buetschliite—strong
Dolomite, 75 Calcite, 25	Not X-rayed	Calcite—moderate Dolomite—strong Brucite—moderate Portlandite—moderate Buetschliite—moderate
Dolomite, 50 Calcite, 50	Calcite—strong Dolomite—strong Brucite—weak Portlandite—not discernible Buetschliite—not discernible	Calcite—moderate Dolomite—strong Brucite—moderate Portlandite—strong Buetschliite—strong
Dolomite, 25 Calcite, 75	Not X-rayed	Calcite—very strong Dolomite—moderate Brucite—trace Portlandite—strong Buetschliite—strong
Calcite, 100	Calcite—dominant Dolomite—not discernible Brucite—not discernible Portlandite—trace Buetschliite—not discernible	Calcite—very strong Dolomite—not discernible Brucite—not discernible Portlandite—strong Buetschliite—strong

formation of calcite accompanying the breakdown of pure dolomite at Eq. OH$^-$/Eq. CO$_3^=$ of 0.50 or lower, and (b) the formation of brucite wherever dolomite has been attacked. An additional phase produced by these reactions, but not evident in the equivalent NaOH reactions, is $Ca(OH)_2$, or portlandite. In concrete this $Ca(OH)_2$ together with the $Ca(OH)_2$ produced by hydrating cement might slow or even halt the reaction according to the law of mass action. The chemical equations which explain the reaction products given in Tables 2 and 4 are developed in the following section.

As noted earlier, it appears that equilibrium has not been attained in these mixtures. This is indicated by a variation in the previously discussed mass changes and in the amount of reaction products shown by duplicate KOH-mineral soaks. Also, it is noteworthy that very strong dolomite peaks are still evident after 20 weeks in mixtures containing equal equivalents of KOH and dolomite. As previously mentioned, this peak had completely disappeared in the NaOH soaks of equal concentration in less than 22 weeks.

Chemical Reactions

Following the identification and semi-quantitative analyses of the solid portions of the hydroxide-mineral soaks given in Tables 3 and 4, the filtrates were allowed to evaporate at room temperature. The precipitates thus obtained were identified by X-ray diffraction to be dominantly hydrous alkali carbonates and hydroxides. Inasmuch as both the compounds which went into these reacting systems and those present after reaction were then known, the following significant chemical equations in these systems could be developed

Reaction equations involving NaOH:

$$\underset{\text{Dolomite}}{\mathrm{CaMg(CO_3)_2}} + \underset{\text{Concentrated}}{\mathrm{2NaOH}} + \mathrm{5H_2O} \rightarrow \underset{\text{Brucite}}{\mathrm{Mg(OH)_2}} + \underset{\text{Gaylussite}}{\mathrm{CaNa_2(CO_3)_2 \cdot 5H_2O}} \tag{1}$$

$$\underset{\text{Dolomite}}{\mathrm{CaMg(CO_3)_2}} + \underset{\text{Dilute}}{\mathrm{2NaOH}} \longrightarrow \underset{\text{Brucite}}{\mathrm{Mg(OH)_2}} + \underset{\text{Calcite}}{\mathrm{CaCO_3}} + \mathrm{Na_2CO_3} \tag{2}$$

$$\underset{\text{Calcite}}{\mathrm{2CaCO_3}} + \underset{\text{Concentrated}}{\mathrm{2NaOH}} + \mathrm{5H_2O} \longrightarrow \underset{\text{Gaylussite}}{\mathrm{CaNa_2(CO_3)_2 \cdot 5H_2O}} + \mathrm{Ca(OH)_2} \tag{3}$$

Reaction equations involving KOH:

$$\underset{\text{Dolomite}}{\mathrm{18CaMg(CO_3)_2}} + \underset{\text{Concentrated}}{\mathrm{44KOH}} + \mathrm{42H_2O} \rightarrow \underset{\text{Buetschliite}}{\mathrm{7Ca_2K_6(CO_3)_5 \cdot 6H_2O}} + \underset{\text{Brucite}}{\mathrm{18Mg(OH)_2}} + \mathrm{4Ca(OH)_2} + \mathrm{K_2CO_3} \tag{4}$$

$$\underset{\text{Dolomite}}{\mathrm{CaMg(CO_3)_2}} + \underset{\text{Dilute}}{\mathrm{2KOH}} \longrightarrow \underset{\text{Brucite}}{\mathrm{Mg(OH)_2}} + \underset{\text{Calcite}}{\mathrm{CaCO_3}} + \mathrm{K_2CO_3} \tag{5}$$

$$\underset{\text{Calcite}}{\mathrm{6CaCO_3}} + \underset{\text{Concentrated}}{\mathrm{8KOH}} + \mathrm{6H_2O} \longrightarrow \mathrm{4Ca(OH)_2} + \underset{\text{Buetschliite}}{\mathrm{Ca_2K_6(CO_3)_5 \cdot 6H_2O}} + \mathrm{K_2CO_3} \tag{6}$$

Notes:

(a) Eqs. 2 and 5 were originally proposed by Hadley (6).

(b) Eq. 4 was developed to explain the observed reaction products by combining the following two equations for the reactions which are thought to take place:

$$\mathrm{3CaMg(CO_3)_2} + \mathrm{6KOH} + \mathrm{6H_2O} \rightarrow \mathrm{Ca_2K_6(CO_3)_5 \cdot 6H_2O} + \mathrm{3Mg(OH)_2} + \mathrm{CaCO_3}$$

$$\mathrm{8KOH} + \mathrm{6CaCO_3} \longrightarrow \mathrm{4Ca(OH)_2} + \mathrm{Ca_2K_6(CO_3)_5 \cdot 6H_2O} + \mathrm{K_2CO_3}$$

(c) In accordance with Hadley's (6) theory, the $Ca(OH)_2$ evolving during cement hydration could react with the alkali carbonate (and the hydrated double salts) shown on the right side of these equations, in more or less degree, to produce more alkali in solution.

It should be noted that these equations are based on the formation of reaction products in system open to the atmosphere.

Stability Reactions

Unlike the system Ca, Mg, CO_3, H_2O, the stability relations which have received a great deal of attention from geochemists, the similar systems Na, Ca, CO_3, H_2O and K, Ca, CO_3, H_2O, which are of major interest in the alkali-carbonate reactions, are only slightly known.

Only these two systems are discussed in this work, because the extreme insolubility of $Mg(OH)_2$ would normally serve to remove magnesium ions from solution in concrete. In one of the earliest references found on reactions in the system Na, Ca, CO_3, H_2O, Pratolongo (11) reports that at normal temperatures a 5 percent solution of Na_2CO_3 will react with $CaCO_3$ to produce gaylussite as a stable phase only when Na_2CO_3 is in solution in amounts greater than 14 percent. Also they determined that the gaylussite-pirssonite

($CaNa_2(CO_3)_2 \cdot 2H_2O$) join is at approximately 38 C with the pirssonite phase above this temperature, which indicates that pirssonite would not form at ordinary environmental temperatures. However, Lea and Desch (7) report temperatures in excess of this figure during maximum hydration of some mass concrete. Berg and Borisova (2), working on the solubility isotherms in the system Ca, Na, CO_3, H_2O, give the relative solubilities of calcium and sodium bicarbonates and the composition of the appropriate solid phase in equilibrium at normal temperature. These solid phases are progressively $CaCO_3$, $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $NaHCO_3$ as $Ca(HCO_3)_2$ decreases and $NaHCO_3$ increases in solution.

The system K, Ca, CO_3, H_2O has received very little attention in the literature. Milton and Axelrod (8), in their work on fused wood-ash stones, verified the presence of phases $Ca_2K_6(CO_3)_5 \cdot 6H_2O$ and $CaK_2(CO_3)_2$ and named them buetschliite and fairchildite, respectively, after earlier workers in this system. They observed the slow alteration of fairchildite to buetschliite in the presence of moisture at normal temperature but give no further details on the stability relationships over a range of temperatures and concentrations.

In general it is felt that the reactions in the present work are in good agreement with information available in published works. That gaylussite and buetschliite should occur when the hydroxide solutions are concentrated and not occur when the hydroxide solutions are dilute, would be expected, if, as shown by Hadley (6) and substantiated in this work, dolomite is broken down and magnesium in the form of $Mg(OH)_2$ is removed from the system. This would result in the formation of the alkali carbonate which in turn would react with the $CaCO_3$, present as calcite or as a reaction product from the dolomite, in a manner consistent with that noted in the published data. However, that there may be difficulties in attaining equilibrium in these systems is indicated by discrepancies that exist between the findings of Pratolongo (11) and that of Bury and Redd (4) regarding the amount of Na_2CO_3 required to react with $CaCO_3$ to form gaylussite, and in the difficulties experienced in the present study in obtaining consistent data on mass and volume changes when dolomite and calcite were exposed to KOH solutions.

IDENTIFICATION OF REACTION PRODUCTS IN CARBONATE ROCKS EXPOSED TO ALKALI

The transition from the high surface area to mass ratios which characterizes the minerals and rocks in powdered form to the low surface area to mass ratios of aggregate particles radically alters the rates, and possibly the types, of reactions. To evaluate the data obtained in the studies of finely ground materials, a series of investigations were made on rock prisms and aggregates with much less surface exposed to the alkali environment.

The major difficulty involved in this portion of the study was in the identification of the very small amounts of the reaction products available. Chemical analyses and chemical beneficiation treatments cannot be used in determining the reaction products because of the similar chemistry of the carbonate minerals and the material being sought. Optical and X-ray diffraction studies appear to hold the most promise, if proper techniques can be developed. The major effort in this work has involved X-ray methods.

Laboratory Prisms

Based on the very clear results obtained with the finely divided mineral and rock powders, the following compounds were accepted as the major phases to be sought: sodium and potassium carbonates, brucite, gaylussite, and buetschliite. A number of rock prisms $\frac{1}{4}$ by $\frac{1}{4}$ by $1\frac{1}{4}$ in., which had been used in expansion studies and exposed to 1N NaOH for one year, was selected for study. The composition of the surface layers was identified by X-ray diffraction. Table 5 shows that brucite and gaylussite were clearly evident in the expansive prisms and not evident in the two non-expansive ones.

TABLE 5

X-RAY EVIDENCE OF BRUCITE AND GAYLUSSITE IN CARBONATE ROCK MATERIAL EXPOSED TO NaOH

Aggregate	8-Week Prism Expansion	Powder		Prism	
		Brucite	Gaylussite	Brucite	Gaylussite
12-9	1.04	Moderate	Moderate	Moderate	Trace
12-4	0.78	Moderate	Moderate	Moderate	None
1-8	0.69	Strong	Strong	Moderate	Trace
5-1	0.13	Moderate	Strong	Moderate	Moderate
39-4	0.00	Not run		None	None
13-6	-0.01	Not run		None	None

Field Concrete

In addition to the investigation of the laboratory-treated materials, considerable effort was expended toward finding reaction products in the aggregate from distressed field concrete. Two 4-in. cores were taken from each of two structures which were known to contain reactive rock and which had shown cracking and evidence of expansion. These cores, designated W-1 and C-2, were broken in the laboratory and several samples of the fresh rock were scraped from the areas adjacent to the aggregate-mortar interface. These materials were X-rayed several times utilizing maximum settings on both the log and linear scales. One sample yielded a small peak at $28°2\theta$ which is the major peak for gaylussite. Upon heating for three hours at 200 C, the peak, instead of disappearing, increased in size; this indicated that the material was not gaylussite and its identity is as yet undetermined. All of the other suspected reaction products were checked with negative results, except for brucite, which appeared to be present in trace amounts.

The second method attempted was that of heavy media separation of the lighter reaction products from the remainder of the aggregate using bromoform-benzene solutions with specific gravities of 2.50 and 2.60. The finely ground aggregate in these liquids was allowed to settle, then the upper levels of the solid material were removed and analyzed by X-ray diffraction. Again the results were either negative or, at best, inconclusive.

Inasmuch as these attempts to identify the suspected reaction products were unsuccessful, a completely different approach to the problem was made. Several grams of clean aggregate fragments were taken from concretes W-1 and C-2. This material was powdered and carefully sieved. A 3-gm sample of the minus 200 to plus 325 portion was weighed to the nearest 0.0001 gm. The same procedure was carried out for a piece of the same aggregate type (1-8) which had been taken directly from the quarry. Each of the 3-gm samples was then put into 100 ml of hot distilled water and agitated for 10 min. The suspension was filtered, dried and weighed. This whole procedure was performed three times with the results given in Table 6.

These differences, while not great, appear to be consistent and are interpreted to indicate the presence of small amounts of relatively soluble reaction products in the aggregate from the concrete. To check this, the filtrates of two of the soaks were allowed to evaporate and the third was analyzed for calcium, sodium, and potassium in solution; the results are given in Table 7.

Table 7 shows that significant amounts of the alkalies from the cement have migrated into the aggregate. Finally, the residue from the evaporated filtrates was identified by X-ray diffraction using the powder camera. The calcium carbonate pattern was strong in each film. However, samples C-2 and W-1 each contained d-values indicative of the bicarbonates or hydrous carbonates of potassium and sodium. It is interesting

TABLE 6

WEIGHT LOSS (Percent) IN HOT DISTILLED WATER

Sample	First Run	Second Run	Third Run	Average
Quarry rock (1-8)	1.18	1.11	1.38	1.22
Concrete aggregate (C-2)	1.23	1.32	1.50	1.35
Concrete aggregate (W-1)	1.40	2.11	1.48	1.66

TABLE 7

ANALYSES OF FILTRATES

Sample	PPM in 100 Ml Filtrate		
	Calcium	Sodium	Potassium
Quarry rock (1-8)	7.0	1	7.5
Concrete aggregate (C-2)	4.5	9.8	29.9
Concrete aggregate (W-1)	7.0	3.5	21.0

to note that in samples C-2 and W-1 calcium carbonate predominated in the X-ray diffractogram, despite the fact that according to Table 7 sodium and potassium salts were probably present in greater amounts. This observation may explain why the alkali reaction products in affected concrete aggregates are so difficult to identify.

Finally, because the concretes represented by samples C-2 and W-1 are now essentially dry in the field, it appears logical to assume that at some stage subsequent to placement of the concrete the alkali concentrations of solutions within the aggregates must have become quite high.

DISCUSSION AND CONCLUSIONS

A principal aim of this work has been to investigate the chemical reactions taking place in open, aqueous systems containing calcite, dolomite, and sodium or potassium hydroxide. The breakdown of dolomite and the resulting volume and mass changes which take place were observed throughout a range of hydroxide concentrations and carbonate types. However, the effect of this breakdown on the actual observed expansion of certain carbonate rocks must be viewed as only part of a complex interplay of variables.

Access of hydroxides and the intrinsic rock strength to resist volume changes, resulting from the nature and geometry of grain boundaries, are of primary importance in determining rock expansion. In addition, the environment of hydrating cement in concrete superimposes a complex chemistry over the alkali-aggregate reaction which may radically alter the reaction rate and the formation of certain phases. Until these other parameters have been investigated in detail, the relative effects of each variable considered in this work must remain as a matter of conjecture.

The data presented here, tempered in light of earlier work, are thought to justify the following conclusions:

1. Quartz and clay in the carbonate rocks quarried in Virginia are not appreciably affected in the expansive alkali reaction of the host rock.

2. Finely ground dolomite and calcite minerals and carbonate rocks increase in volume and mass when exposed to NaOH and KOH solutions.

3. The amount of apparent volume and mass increases is directly related to the dolomite content for any given concentration of NaOH, whereas increases in volume and mass for the various carbonate mixtures are nearly equal for a given concentration of KOH.

4. The volume and mass change is accompanied by the breakdown of the mineral dolomite where this mineral is present.

5. In the open systems (exposed to air) used in this study the breakdown of dolomite yields calcite and brucite in low concentrations of NaOH and KOH; i.e., when Eq. OH^-/Eq. $CO_3^=$ = 0.50, and brucite and gaylussite or buetschliite in high concentrations; i.e., when Eq. OH^-/Eq. $CO_3^=$ = 0.75.

6. Brucite and gaylussite have been identified at prism surfaces of reactive rock soaked in NaOH in the laboratory.

7. Brucite has been tentatively identified in the aggregate from distressed field concrete.

8. Analyses of rock from distressed concrete and identical rock directly from the quarry showed significantly higher concentrations of Na and K in the aggregate from the concrete.

9. X-ray diffraction identification of residues obtained by, soaking filtering and evaporating the filtrate of powdered aggregate from distressed concrete indicates the residue to contain $CaCO_3$ and some mixture of bicarbonates and hydrous carbonates of sodium and potassium. As of this writing, however, the exact nature of the sodium and potassium bearing phases in the reacted aggregate is unknown.

10. The identification of high volume, low specific gravity phases, such as gaylussite $CaNa_2(CO_3)_2 \cdot 5H_2O$ and buetschliite $Ca_2K_6(CO_3)_5 \cdot 6H_2O$, and the indirect evidence that hydrated carbonates and bicarbonates of sodium and potassium may occur in alkali-carbonate systems appears to provide a rational mechanism for observed carbonate rock expansions.

ACKNOWLEDGMENTS

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Carbonate Aggregate Reactions: Recent Studies and an Approach to the Problem

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The results of some recent studies on carbonate aggregate reactions are presented and the approach to the problem of deleterious behavior of certain varieties of carbonate rocks in concrete through a systematic study of highway concrete is described.

Expansion studies were made on a variety of carbonate rocks occurring in Iowa. Data obtained from the alkali-expansion test of carbonate rocks were classed into four categories similar to those of Newlon and Sherwood: (a) A few rocks with expansion greater than 0.5 percent; (b) Some rocks with expansion between 0.0 - 0.5 percent; (c) A few rocks with reversed behavior—a preliminary contraction followed by expansion not exceeding 0.5 percent; and (d) The majority of the rocks which contracted. Quantitative calcite-dolomite X-ray diffraction analysis of the rocks involved in expansion studies indicates that the rocks containing dolomite dedolomitize to some degree in alkaline solutions regardless of whether they expand or contract (Table 3). Preliminary studies show that an apparent relationship may exist between the amount of expansion (or contraction) and the initial effective porosity. Rocks with higher effective porosities (> 8%) contracted; those with lower effective porosities (8% or less) expanded. The results to date favor a causative mechanism of expansion most closely related to rock texture and pore structure of the rock.

Additional research on the effect of the reaction environment (method of inducing the reaction) on the behavior of silica was studied by embedding cores of selected aggregate in 2- by 4-in. mortar cylinders and then reacting the cylinders in a series of environments including: (a) autoclaving at 220 F for 1 week; (b) hot water bath at 55 C for 3 months; (c) storage at high humidity at 55 C for 3 months; (d) storage at high humidity at room temperature for 1 year; and (e) paraffin coated, storage over water of room temperature for 1 year. The results (Table 4) indicate that rocks react in all environments and the degree of reaction varies with intensity of the environment. The importance of moisture is also emphasized. The rocks show a relative gain in silica (insoluble residue) content for environments a, b, and c. All rocks show a relative decrease in environments d and e. For comparative purposes one could consider that natural non-winter environment of highway concrete to approximate in part the range of experimental environments b, c, and d. The work suggests that in future studies attention should be paid to the method of inducing reaction in carbonate rocks.

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An approach to the problem of why certain carbonate aggregates are related to distress in concrete has been undertaken through a study of highway concrete in order to learn more about the change in the entire system: coarse aggregate, and the fine aggregate-cement paste matrix. A chronological sequence of cores was taken from concrete highways with good service records made from the same coarse aggregate and this was also done with concretes having poor service records. Some cores of the same age but showing variation in concrete condition related to variation in aggregate were also taken. Systematic X-ray diffraction, chemical, and petrographic techniques are being used to study the matrix and coarse aggregate of the concrete. The sonic modulus and compressive strengths of the cores are also being measured as part of the program. It is hoped that this study of concretes of varying ages with good and poor service records will provide: (a) a basis for understanding how rocks contribute to distress in concrete; and (b) better knowledge of the "changes" or "aging" which occurs in concrete. Such information is essential to establish the causative mechanism(s) of distress.

•CONSIDERABLE interest exists concerning the general problem of behavior of carbonate aggregates in concrete. A principal objective of researchers in this area is an understanding of how carbonate rocks contribute to distress in concrete. Although progress has been made (i.e., recognition of expansive carbonate rocks) through the contributions of many, attainment of this objective will require more research in several areas. Two principal areas are (a) continued research on the reactivity of carbonate rocks having differing properties and service records in alkaline (high pH) environments, and (b) a broader and more integrated view of the various aspects of the problem as it exists in different parts of the country.

The purpose of the first section of this paper is to review recent studies on alkali reactivity of carbonate rocks and present additional data on this subject. The specific areas are (a) expansion studies, and (b) environmental effects on carbonate reactions.

In the last section of the paper a brief summary of some aspects of the problem of carbonate aggregate behavior in Iowa is given to provide an understanding of the current research effort on the "aging" of highway concretes with both good and poor service records.

EXPANSION STUDIES

This study was undertaken on a variety of carbonate rocks occurring in Iowa to determine their expansion behavior by techniques used in similar studies by Swenson and Gillott (1), Hadley (2), and Newlon and Sherwood (3). Another purpose of this study was to investigate the feasibility of applying the relatively simple techniques required in conducting expansion studies as a possible new test for evaluating carbonate rocks.

Rocks Sampled

The carbonate rocks utilized were obtained from 9 quarries in central and eastern Iowa (Table 1). An additional sample of rock from Virginia was supplied by W. Cullen Sherwood of the Virginia Council of Highway Investigation and Research. In selecting the rocks an attempt was made to secure a variety of carbonate rocks with differing lithology and service records. The rocks currently considered to have good service records when used in highway concrete are those from the Dubuque, Linwood (except for beds 16 and 17, Solon Member), River Products, and Ferguson (beds 11-16 only, Eagle City Member) quarries. Rocks with poor service records are those from the Earlham, Glory, and LeGrand quarries. The Douds and Otis quarries are considered in a doubtful category as far as service record is concerned and recently serious consideration has been given to stop further use of Otis stone in highway concrete.

TABLE 1

QUARRIES SAMPLED

Quarry	Location	Geologic Age	Stratigraphic Position	Beds Sampled[1]
Douds	Douds, Van Buren Co.	Middle Miss.	St. Louis Fm.	6, 7A, 7B, 8A, 10A, 10B, 11A, 11B, 12
Dubuque	Dubuque, Dubuque Co.	Middle Ordovician	Prosser member, Galena Fm.	1, 3, 4
Earlham[2]	Earlham, Madison Co.	Upper Penn.	Bethany Falls member, Swope Fm.	4, 5, 6
Ferguson	Ferguson, Marshall Co.	Lower Miss.	Eagle City and Maynes Creek[3] member, Hampton Fm.	2[3], 4[3], 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 19
Glory[2]	Blackhawk Co.	Upper Devonian	Rapid member, Cedar Valley Fm.	2, 3, 4, 5, 6, 8, 9, 10
LeGrand[2]	LeGrand, Marshall Co.	Lower Miss.	Maynes Creek member, Hampton Fm.	8, 9, 10, 11, 12, 13
Linwood	Buffalo, Scott Co.	Middle Devonian	Otis and Davenport members, Wapsipinicon Fm.; Solon[3] member, Cedar Valley Fm.	3, 4, 6, 9, 10, 11, 13, 14, 16[3], 17[3]
River Products	Iowa City, Johnson Co.	Upper Devonian	Coralville member, Cedar Valley Fm.	1, 4, 6
Otis[2]	Cedar Rapids, Linn Co.	Middle Devonian	Otis member, Wapsipinicon Fm.	2, 3, 6, 8A, 8B

[1] Bed numbers as shown correspond with stratigraphic sections on file at the Iowa State Highway Commission with the exception of the Linwood quarry.

[2] No longer used as aggregate source.

[3] Denotes member samples occur in.

Sample Preparation

The samples were prepared from a representative slab of rock taken from individual beds in the nine quarries. Two flat surfaces parallel to bedding and 2 in. apart were cut on each slab. Cores ½ in. in diameter and 2 in. in length were rapidly drilled normal to bedding with a diamond bit mounted on a drill press. Six cores were taken from each block according to a pattern in which the cores were spaced at approximately 1 in. centers around the perimeter of a 45° triangle. The three cores located at the vertices of the triangular pattern were pulverized and thoroughly mixed to provide a sample for wet chemical and X-ray diffraction analysis. The three cores located at the midpoint of each side were used for expansion measurements after 45° tapers were ground at the ends with an emery wheel.

Experimental Methods

Each sample was analyzed for its major chemical constituents, initial dolomite content and initial effective porosity. Two cores from each bed were immersed in solutions of 1.0 normal sodium hydroxide; a third was stored in distilled water as a control. Length changes were measured for periods of up to 7 months. At the end of this period certain samples which displayed characteristic behaviors in the alkaline solution were selected for further studies. Additional parameters considered were macroscopic and microscopic textural features, acid-insoluble residue composition, final dolomite content, and final effective porosity.

The wet chemical analyses for calcium, magnesium, silicon and insoluble residue of each sample were determined according to the method of Bisque (4).

Initial and final dolomite contents were determined by a quantitative X-ray diffraction technique according to the method of Handy (5). A General Electric diffractometer incorporating a scintillative counter and pulse height discriminator was used. Peak intensities were measured by cumulative counting across the peaks during a 20 scan with

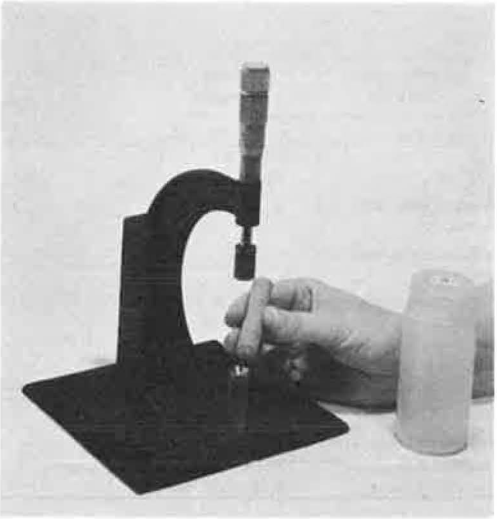

Figure 1. Specially adapted micrometer gage adjacent to a tapered core of rock and polyethylene bottle containing alkaline solution.

the count total being automatically printed out at the end of the scan. Samples were ground to a particle size of less than 1 micron in a vibratory impact grinder. The sample mounts were pacted under a standard pressure of 1,000 psi and rotated during the scan to detect any preferred orientation effects. A calibration curve was prepared from calcite-dolomite mixtures varying by 10 percent increments over the range of 0-100 percent.

Effective porosities were calculated from data obtained with a Ruska mercury capillary apparatus.

The measurement of expansion of the cores was made with a mounted micrometer with end plugs (Fig. 1) which accepted a 45° taper. The instrument was calibrated with a 1.760-in. invar steel cylinder. The three expansion cores were stored for 24 hr in 150 ml of distilled water before an initial length reading was recorded. Following the initial reading, two cores were transferred to individual airtight polyethylene bottles containing 150 ml of 1.0 normal sodium hydroxide. The third was left in water as a control. Before each measurement the cores were rinsed in distilled water and surface-dried. Four readings for each core were obtained by rotating through 90° steps in the micrometer. Readings were reproducible within 0.001 in. and expansion expressed as percent of initial length agreed within 0.025 percent for duplicate cores.

Textures were studied by means of polished sections using a reflecting microscope.

Experimental Results

Expansion.—The data on all the samples from nine quarries are presented in Table 2. The insoluble residue, calcium, magnesium, and silicon contents are presented with the expansion data obtained after 150 days in sodium hydroxide solution.

On the basis of rate and extent of expansion after an arbitrarily chosen period of 150 days, it was possible to assign the samples studied to one of four categories:

Category I—samples which expanded in excess of 0.5 percent.
Category II—samples which expanded between 0.0 and 0.5 percent.
Category III—samples which contracted prior to expanding.
Category IV—samples which contracted steadily.

Data pertinent to these samples are presented in Table 3 and in Figures 2-9. The sample numbers used in Table 3 are also used in Figures 2-9 to facilitate graphical presentation.

Relationship of Expansion to Bedding Plane Orientation.—The expansion results plotted in Figures 2-5 were obtained from samples cut length-perpendicular to apparent bedding features. It was necessary to determine what effect planes of weakness such as clay seams may have had on the observed expansion. Six of the original bedding plane slabs from the Glory quarry were used. In this instance samples were cut length-parallel to bedding. Expansion results over a period of 75 days are presented in Figure 6. The prime superscript aids comparison with corresponding samples in Figures 2-4. Specimens cut normal to bedding expanded considerably more than those cut parallel to bedding.

Texture.—Hand specimens for each sample included in Table 2 were described as medium to tan to gray, finely crystalline dolomitic limestones. Many appeared to be

TABLE 2

ANALYSES OF ROCK PRIOR TO ALKALI TREATMENT AND EXPANSION DATA

Quarry	Bed	Residue Wt. (%)	Ca as $CaCO_3$ Wt. (%)	Mg as $MgCO_3$ Wt. (%)	Si as SiO_2 Wt. (%)	Expansion[1] (%)
Doud	6	2.8	95.3	1.5	1.9	-0.1
	7A	8.3	56.8	32.9	5.7	0.0
	7B[2]	11.6	49.9	36.8	7.9	0.2
	8A	2.7	96.6	0.4	1.5	-0.1
	10A	22.9	44.0	31.6	19.7	-0.2
	10B[2]	14.5	66.6	17.0	10.2	0.4
	11A	2.6	57.8	39.4	1.6	0.0
	11B	2.6	54.4	41.2	1.9	-0.1
	12	4.4	64.8	29.3	2.8	0.0
Dubuque	1	3.5	92.9	3.0	3.1	-0.1
	3	15.5	45.0	38.8	12.9	-0.2
	4[2]	3.3	51.6	44.3	2.3	-0.2
Earlham	4	13.4	81.3	3.6	12.1	-0.1
	5	7.3	88.0	3.8	6.3	-0.1
	6[2]	26.7	61.0	10.5	21.0	1.2
Ferguson	2	1.8	89.3	9.0	1.7	-0.1
	4[2]	7.1	52.6	38.6	5.2	-0.1
	6	0.8	93.8	5.3	0.6	-0.1
	7[2]	11.2	50.6	36.1	7.5	0.1
	9	1.6	71.3	23.9	0.4	-0.2
	10	2.7	63.0	33.2	2.1	-0.1
	11	3.2	62.0	33.4	2.1	-0.1
	12	1.9	95.1	2.2	1.7	-0.1
	13	2.8	64.8	31.2	1.9	-0.1
	14	1.4	78.8	18.3	1.1	-0.1
	16	1.3	89.0	8.6	1.7	-0.2
	17	1.4	78.3	19.1	1.7	-0.2
	19	1.9	59.9	36.5	1.2	-0.2
Glory	2[2]	7.2	66.5	24.8	5.2	0.8
	3[2]	10.1	65.2	23.4	6.8	1.2
	4[2]	10.9	60.9	26.1	7.5	0.4
	5[2]	12.1	61.9	23.9	8.6	1.1
	6[2]	12.8	62.9	22.1	9.2	0.8
	8[2]	9.1	68.4	20.7	6.9	0.2
	9	15.9	53.3	28.4	11.2	0.0
	10[2]	16.1	50.3	31.5	11.7	0.1
LeGrand	8	2.7	57.4	37.7	1.9	0.0
	9	2.6	56.1	39.0	1.9	0.0
	10	1.6	70.3	26.3	1.5	0.0
	11	1.6	64.1	31.9	1.6	0.0
	12	2.0	62.0	34.1	1.7	0.0
	13	1.0	82.0	15.0	1.3	0.0
Linwood	3	0.4	97.0	1.9	0.6	-0.1
	4	0.8	98.3	0.4	0.7	-0.1
	6	0.7	97.1	1.6	0.3	-0.1
	9	1.2	96.8	1.6	0.9	-0.2
	10	0.0	97.3	1.5	1.3	-0.1
	11[2]	6.4	78.8	13.3	1.6	-0.2
	13	2.4	91.8	5.1	1.7	-0.1
	14	0.9	96.8	1.2	1.2	-0.2
	15	2.6	85.5	9.9	1.9	-0.1
	16	3.7	89.3	5.5	2.6	0.0
	17[2]	9.7	76.3	11.0	7.7	0.5
Otis	2	1.6	77.5	19.0	2.0	-0.1
	3	1.2	53.0	44.9	1.0	-0.2
	6	1.7	53.3	43.6	1.3	-0.2
	8A	0.2	52.8	45.7	0.8	-0.3
	8B	0.3	52.6	44.4	0.2	-0.2
River Products	1	0.1	95.0	5.1	0.5	-0.3
	4	0.3	96.6	2.3	0.4	-0.2
	6	1.9	97.9	2.2	1.0	-0.1

[1] 150 days in NaOH.

[2] Denotes samples selected for further study (see Table 3).

TABLE 3

CARBONATE ROCK DATA

Sample No.	Quarry and Bed	Residue Wt. (%)	Dolomite[1] Wt. (%)		Dolomite Reacted Wt. (%)	Expansion After 150 Days (%)
			Initial	Final		
(a) Category I - Expansion Greater than 0.5%						
1	Earlham-6	26.7	24	11	54	1.21
2	Glory-3	9.9	62	32	44	1.18
3	Glory-5	11.0	66	42	36	1.05
4	Virginia 1s	25.1	70	64	9	0.97
5	Glory-6	13.2	63	54	14	0.83
6	Glory-2	6.1	54	39	29	0.77
(b) Category II - Expansion Between 0.0-0.5%						
7	Linwood-17	9.7	21	4	81	0.45
8	Doud-10B	14.5	77	32	59	(0.38)[2]
9	Glory-8	9.6	45	24	47	0.21
				Average 41		
(c) Category III - Expansion Preceeded by Contraction						
10	Glory-4	10.8	52	46	12	0.39
11	Doud-7B	11.6	87	58	33	(0.15)
12	Ferguson-7	11.4	89	82	8	0.12
13	Glory-10	16.2	84	61	27	0.11
(d) Category IV - Steady Contraction (typical samples)						
14	Ferguson-4	7.1	93	93	0	-0.10
15	Dubuque-4	3.3	97	95	2	-0.19
16	Linwood-11	6.4	30	15	50	-0.20
	LeGrand-8	2.7	92	90	2	-0.01
	LeGrand-9	2.6	92	64	30	-0.01
	LeGrand-11	1.6	85	43	49	-0.03
	LeGrand-12	2.0	90	65	28	0.01
	Doud-7A	8.3	80	42	48	-0.01[2]
	Doud-12	4.4	70	17	76	-0.01
	Otis-2	1.6	86	24	33	-0.15[3]
	Otis-6	1.7	98	74	24	-0.23
	Otis-8B	0.3	0.000[4]	0.004[4]	—	-0.17
	Ferguson-9	1.6	66	45	24	-0.36
	Ferguson-10	2.7	88	67	26	-0.14
	Ferguson-14	1.4	38	28	26	-0.10
	Ferguson-19	1.9	90	33	63	-0.22

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[1] Dolomite content determined by quantitative X-ray methods (Moore). Represents dolomite content of the rock.

[2] Samples stored 13 months in sodium hydroxide solution.

[3] Samples stored 15 months in sodium hydroxide solution.

[4] Calcite: dolomite count ratios.

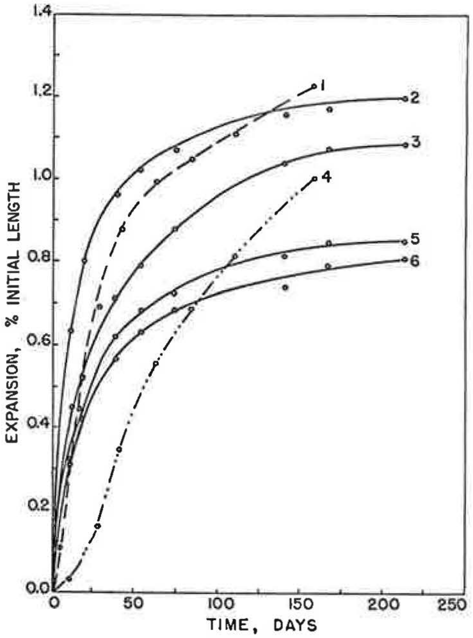

Figure 2. Rate of expansion curves for samples assigned to category I.

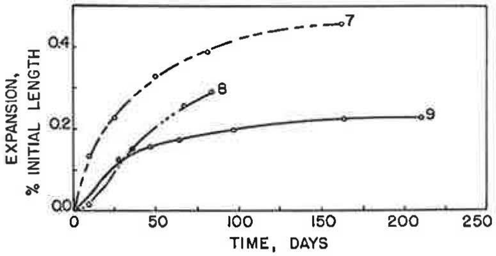

Figure 3. Rate of expansion curves for samples assigned to category II.

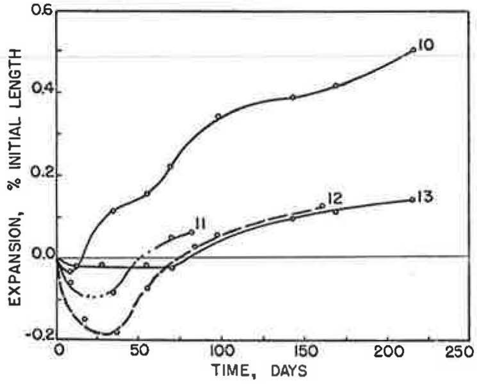

Figure 4. Rate of expansion curves for samples assigned to category III.

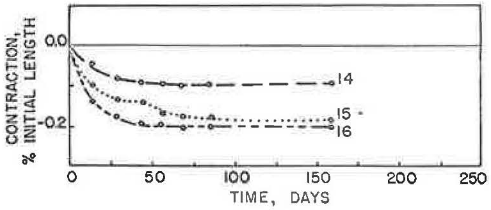

Figure 5. Typical rate of contraction curves for samples assigned to category IV.

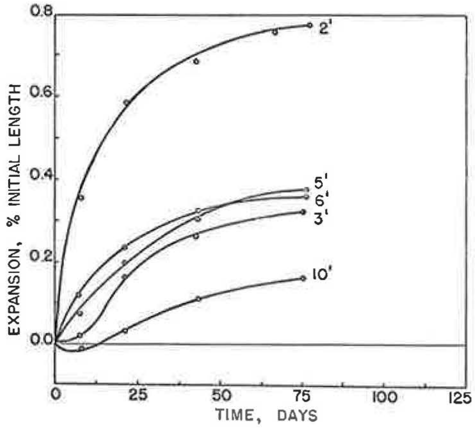

Figure 6. Rate of expansion curves for samples from Glory quarry cut length-parallel to apparent bedding features.

TABLE 4

EFFECTIVE POROSITY OF SELECTED CARBONATE SAMPLES

Category	Sample No.	Effective Porosity (%) Initial	Effective Porosity (%) Final
I	1	7.29	—
	2	7.12	3.66
	3	4.28	3.22
	4	4.25	3.53
	5	5.77	4.08
	6	7.73	3.47
II	9	10.01	3.94
III	10	4.63	3.61
	12	6.63	3.90
	13	13.17	9.23
IV	14	9.27	2.30
	15	9.38	5.75
	Earlham-4	13.47	—
	Glory-9	9.80	5.56

argillaceous. The samples from the Glory quarry were finely laminated. The Earlham-6 sample was an interbedded carbonate-lutite.

Microscopic examination of polished sections showed the samples to consist of varying proportions of: (a) euhedral to subhedral dolomite rhombs 25-75 microns in length; (b) subhedral to anhedral dolomite fragments or irregular crystals averaging less than 25 microns in length; and, (c) a micro crystalline matrix composed of carbonates and clay-sized silicate material. Progressive inspection of samples in category I through category IV revealed a steadily decreasing proportion of small anhedral carbonate fragments. The contracting samples assigned to category IV were characteristically dense, interlocking carbonate mixtures.

Composition of Acid-Insoluble Residue.—Quartz and illite were the only minerals positively identified in the non-carbonate fraction of the samples. Silt to clay-sized quartz was the major constituent of each residue examined.

Effective Porosity.—The initial and final effective porosities of the samples studied in detail are given in Table 4. Several contracting samples not listed in Table 2 have been added. The initial effective porosity has been plotted against expansion in Figure 9.

Discussion of Results

One of the striking observations of the study is that most of the rocks (43) contract slightly and only a few (12) expand. These results and the rest of the data, on the whole, tend to confirm the earlier work of Swenson and Gillott (1), Hadley (2), and Newlon and Sherwood (3). Because of the effective porosity data and additional X-ray diffraction determination of the dolomite contents of samples before and after treatment in NaOH, interpretation of these data has led to some different conclusions which are discussed in the following.

The rate of expansion curves (Figs. 2-5) shows that the relative order of expansion for the rocks tested was established (with two exceptions) after a period of 25 days. This suggests a safe lower time limit for any potential aggregate testing procedure based on relative expansion values. The general tendency for the curves to level off in less than 100 days may be related to a reduction in permeability caused by the accumulation of reaction products in the rock pores. This is inferred from the final effective porosity data given in Table 3.

An explanation for the shapes of the curves in Figures 4 and 5 is not obvious to the authors. Newlon and Sherwood (3) suggest that the apparent contraction may be related to the testing procedure: "The placing of a specimen whose pores are filled with water into a solution of sodium hydroxide may be thought of as creating an osmotic pressure wherein the water tends to migrate from the pores into the solution, slightly dehydrating the specimen and producing a measurable contraction." This explanation appears to be inadequate in the present case because all of the reference samples stored in distilled water showed a similar contraction during the period of measurement; i.e., all the samples contracted in distilled water regardless of their behavior in sodium hydroxide solutions.

The expansion values shown in Figure 6 may be compared with corresponding samples in Figures 2 and 4. It is seen that after 75 days cores cut length-parallel to bedding features have expanded at least one-third less than the length-perpendicular samples. Bedding planes appear to enhance the directional character to the release of stress. Swelling and cracking along bedding planes do not account for the bulk of the observed expansions.

The compositions of samples chosen at random from the 43 which showed contraction are also plotted in Figure 7. Although a bell-shaped curve similar to Hadley's (2) was drawn for comparative purposes through the points obtained from samples which expanded, it is equally apparent that rocks with similar compositions contract. From these data alone it would not be possible to predict expansion on the basis of carbonate composition of the whole rock.

Swenson and Gillott (1) were the first to suggest that the expansion of certain carbonate rocks may be the result of a dedolomitization reaction. Hadley (2) and others (12)

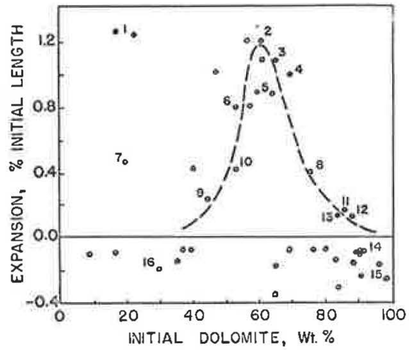

Figure 7. Expansion after 150 days as a function of initial weight percent of dolomite.

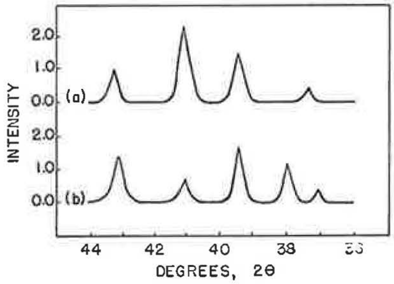

Figure 8. Diffractometer traces of Glory-8 sample: (a) original sample; (b) same sample after residing 200 days in 1.0N NaOH.

concur on this point but as of yet no satisfactory mechanism(s) has been established. Qualitative proof of a dedolomitization reaction is shown in Figure 8. The 38° brucite peak, absent in the "before" trace, appears in the diffractometer trace of a Glory-8 sample after soaking in a 1.0 normal solution of sodium hydroxide for 200 days. The 41° dolomite peak shows an appreciable reduction in intensity, and the brucite peak was the only new reflection observed in any of the "after" samples scanned between 4° and 55° 2θ.

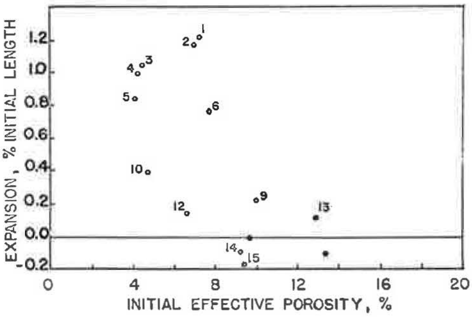

Figure 9. Expansion after 150 days as a function of initial effective porosity.

The results of a quantitative study of dedolomitization are given in Table 3. Although the average "percent dolomite reacted" for categories I and II is 15 percent greater than the average value for categories III and IV, it is evident individual specimens which contract indicate up to 76 percent dolomite reacted. From these data it may be wondered if the rate of dedolomitization could ever be dependent on carbonate composition alone. What is most evident in data of Table 3 is the fact that rocks which contain dolomite dedolomitize in alkaline solution regardless of whether they expand or contract.

An additional point of interest observed concerning the data in Table 3 is the strong relationship of insoluble residue content to expanding and contracting rocks. The first three categories of expanding rocks average 13.5 percent insoluble residue. Category IV, the contracting specimens, average 3.1 percent. Workers elsewhere (1, 2, 3) have found a similar relationship. Lemish et al. (7, 8), in earlier work on rim growth studies, have found that the insoluble residue content of a rock is closely related to its ability to grow reaction rims.

It was earlier noted that the sample assigned to categories I and II contained relatively large proportions of small, anhedral carbonate fragments. It would be expected that the rate of dedolomitization should be related to this texture. The average values of Table 2 support this reasoning. These data suggest that the rate of dedolomitization is generally a function of crystal size and not of a specific carbonate composition. Crystal size is an important rate-controlling factor which deserves further consideration.

The observations regarding textural features of the expansive rocks are in complete agreement with those of other workers (1, 2, 3). Because of this agreement, an attempt was made to relate expansion to physical properties of the samples. In the absence of equipment to measure permeability directly, it was decided to compare the samples on the basis of effective porosity.

Figure 9 shows a tendency for those samples assigned to category I to have a relatively low effective porosity. The contracting samples assigned to category IV are characterized by initial porosities greater by at least 60 percent. This suggests a possible causative mechanism for expansion in which the products of a dedolomitization reaction are effective in producing expansion only when the amount of initially available pore space is inadequate to accommodate their rate of accumulation or migration out of the rock.

ENVIRONMENTAL EFFECTS ON CARBONATE REACTIONS

Introduction

During the course of research on carbonate aggregates, several methods of inducing carbonate aggregate reactions related to formation of silicified rims on certain rocks have been employed at Iowa State University and by others elsewhere.

Bisque and Lemish (6) were the first to induce rim growth by either soaking concrete bars at 140 F for 2 months or alternately soaking them at room temperature for a day followed by oven-drying at 140 F for 24 hr. The autoclave (7) has been successfully employed in the University's laboratory to induce reactions in concrete bars rapidly within a matter of hours or a few days. Bisque (8) also grew silicified rims in aqueous environments by immersing blocks of reactive aggregate in sodium metasilicate solutions. Hiltrop (9) originated and Werner (10) extended a reflux procedure to determine rapidly (48 hr) and quantitatively the "silicon" absorption capacities of small rock chips.

Swenson and Gillott (1) induced reaction in Kingston aggregates by reacting concrete bars at 100 percent humidity at room temperature over a period of months. Hadley has adapted the Bisque and Lemish (8) techniques by reacting prisms of rock embedded in mortar bars and sealed in cans at 100 percent humidity at 100 F for 8 weeks.

It is readily understandable therefore when such a variety of environments has been employed to induce reactions, that the influence or effect of environment on the nature of the reaction be seriously considered a problem in interpretation of experimental results.

Another major problem in the quantitative study of reactions is that of sampling. The sampling of aggregate fragments from highway or laboratory-prepared concretes has been difficult and time consuming. Bisque and Lemish removed aggregate samples from a concrete matrix by chipping and filing. Harwood (11) used a dentist drill to obtain his samples for chemical analysis. Gillott (12) used a chisel and dentist drill to study rimmed aggregates found in concrete. The accuracy of such methods is open to question because destructive testing precludes accurate comparisons of "before" and "after" samples.

In view of these problems, a special study was undertaken to investigate the effect of environments on aggregate silicification and to meet the rigorous requirements caused by the use of destructive tests in "before" and "after" samples. A method of providing samples which meets these requirements was devised and applied to evaluate silicification under closely controlled conditions.

Experimental Approach

Bedding plane slabs from the Burton Avenue, Glory, and LeGrand quarries were cut into 8- by 4- by 2-in. blocks for sampling. Cores 0.5 in. in diameter were taken at 1-in. centers over a rectangular grid with a minimum of 20 cores per slab.

Alternate cores from each column and row of a given slab were individually analyzed for silica content using the method of Bisque (4). The remaining cores were embedded in mortar cylinders 4 in. long and 2 in. in diameter. The cylinders were curved for two days at 100 percent relative humidity and 73 F before being transferred to one of five environments:

Environment A—autoclave (20 psi and 105 C) for one week,
Environment B—in distilled water at 55 C for three months,
Environment C—over distilled water at 55 C for three months,
Environment D—over distilled water at room temperature for 1 year, and
Environment E—paraffin-coated cylinders over water at room temperature for one year.

Cylinders placed in the autoclave stood on the floor of the steam-filled chamber. The cylinders in and over water at 55 C were individually sealed in polyethylene bottles and submerged in a water bath maintained at that temperature. An evacuated desiccator partially filled with water was used to store the samples in the room temperature environment.

Following the specified exposure to each environment, the cylinders were sawed into disks approximately 0.5 in. thick. The disks were broken by tapping firmly at the periphery. The carbonate cores were removed intact and without residual traces of fine aggregate or hydrated cement paste.

The silica contents of the reacted samples were determined. For each sample the final silica content was compared to the average silica content of its "nearest neighbors" in the original block.

Experimental Results

The change in silica content for the samples reacted in environments A, B, C, D, and E is given in Table 5.

TABLE 5

EFFECT OF ENVIRONMENT ON REACTION

Sample	Environment[1]	SiO_2 Wt. (%) Original	After Reaction	Change
Glory	A	11.6	12.5	+0.9
	B	11.2	12.5	+1.3
	C	11.0	11.7	+0.7
	D	12.1	11.2	-0.9
	E	11.7	10.7	-1.0
Burton Ave.	A	3.3	4.4	+1.1
	B	3.0	3.6	+0.6
	C	2.9	3.7	+0.8
	D	3.3	2.7	-0.6
	E	3.0	2.9	-0.1
LeGrand	A	0.9	1.3	+0.4
	B	0.9	1.1	+0.2
	C	0.9	0.8	-0.1
	D	0.9	0.6	-0.3
	E	0.8	0.7	-0.1

[1] Environments:
A = autoclave, 20 psi and 105 C for 1 week.
B = in water at 55 C for 3 months.
C = over water at 55 C for 3 months.
D = uncoated over water at room temperature for 1 yr.
E = paraffin coated over water at room temperature for 1 yr.

Discussion of Results

Two important points which should be emphasized before discussing the results in Table 5 are (a) the reacted samples were recovered quantitatively, and (b) the transfer of silica occurred in the presence of (concrete) pore solutions alone—no bulk/excess water phase was required.

The increase in silica content for the Glory and LeGrand samples is of the same relative order established by Werner (10) using reflux techniques and Bisque (8) with his experiments on chips of rock reacted in ports within mortar bars.

It was earlier noted that rim zones from aggregate fragments reacted in mortar bars were originally separated for analysis by chipping and filing. The representativeness of these samples was questioned (8). In the present work the entire sample was analyzed and no correction is made for the "dilution" effect of unreacted carbonate.

Two important observations can be made from a review of the data given in Table 5: (a) the rocks react in all environments, and (b) the degree and nature of the reaction varies with the intensity of the environment. Although a change in silica content was associated with every environment, the reversal in the silica content related to the environment intensity is of great interest. The rocks show a relative gain in silica content for environments A, B, and C. All the rocks show a relative decrease in environments D and E. Without bulk density data for the specimens before and after the reaction, the actual gain or loss of silica content of the rocks cannot be determined; however, the reversal in the change of silica content does indicate differences in the degree and nature of the reaction as it varies with the environment.

Temperature and moisture are major variables in each environment and it is difficult to state which exerts the greatest effect on the degree and nature of the reaction. Because of previous experience here and elsewhere, the role of moisture is most critical and its importance is emphasized in these experiments.

For comparative purposes, one could consider that natural non-winter environment of highway concrete to approximate in part the range of experimental environments B, C, and D. The work suggests that, in future studies, close attention should be paid to the method of inducing reactions in carbonate rock embedded in mortar.

AN APPROACH TO THE PROBLEM

Recently, as part of the research program on the behavior of carbonate aggregate, a study of highway concretes has been undertaken. To understand this approach, which in essence is a study of how concrete "ages," a brief review of the status of the problem as it exists in Iowa is presented. This is followed by a brief description of the research approach.

Present Status of Problem in Iowa

Although a thorough presentation of the problem is given by Welp and DeYoung (13), some pertinent aspects of it as it is seen today are worthy of review.

The problem can be summarized briefly, as follows: Some rocks fail present acceptance tests and also in service; a few pass present acceptance tests and fail in service; the bulk of the rock used which passes present acceptance tests has a good service record. Rocks with Glory and Earlham characteristics, high insoluble residue dolomites, fail present acceptance tests and are no longer used in service. This would be true of such rocks as the Kingston, Ontario aggregate which is lithologically similar to Glory aggregate in many respects and fails to pass the present ISHC acceptance tests. These reactive and expansive-type rocks are not a present problem and acceptance tests eliminate their use in Iowa.

The aggregates which pass the acceptance tests but have a poor service record are more difficult to categorize. LeGrand rock is an example of this type. Review of service records indicates that rock from the Otis quarry is part of the problem also.

Table 6 was compiled to present some of the similarities and differences of two non-acceptable aggregates related to distress in concrete. Both rocks are dolomitic, contain illitic clay, and have some textural resemblance. In terms of insoluble residue

TABLE 6

PHYSICAL CHARACTERISTICS OF TWO AGGREGATES

Characteristic	Glory Aggregate	LeGrand Aggregate
Texture	Mosaic type	More variable; well-developed crystalline equigranular types predominate; a minor amount of mosaic type occurs
Composition	Calcitic dolomite to dolomitic limestone	Calcitic dolomite
Insoluble residue	Average 12-15%	Average 3%
Clay content	Illitic clay present	Illitic clay present
Reactivity	Highly reactive in concrete environment in terms of rim growth	Slightly reactive in terms of rim growth
Freezing-thawing (water-alcohol) performance	Avg. 30 to 40% loss	Avg. about 4% loss
Silica absorption characteristics	High capacity for silica absorption	Very low capacity for silica absorption
Expansion (soaking rock in alkali)	Expansive—some units expand 1% in 6 weeks	No measurable expansion in 6 weeks time
Dedolomitization (% dolomite reacted)	26[1]	27[2]
Alkali aggregate reactivity-ASTM-C227-52T (% growth-12 mo)	0.03	0.02

[1] Avg. of 7 samples.
[2] Avg. of 4 samples.

content, freezing and thawing performance, reactivity and expansion characteristics in hydroxyl-rich environments, the rocks are noticeably different. Although much has been learned concerning the behavior of the various components of carbonate rocks (i.e., calcite, dolomite, clay, quartz) in alkaline environments, the contrast in properties of these unacceptable aggregates makes it difficult to postulate a direct or indirect mechanism($\overset{S}{?}$) by which aggregates cause distress in concrete.

Another major reason for not understanding the true role of aggregate in concrete distress is the lack of knowledge of what happens to concrete as it ages. Study of deteriorated highway concretes and the present observations by Welp and DeYoung on the performance of concrete pavements have indicated certain trends which point to the necessity for more knowledge concerning changes which take place in the entire system: coarse aggregate and the fine aggregate-cement paste matrix.

Current observations indicating certain trends (13) which appear to have validity can be summed up as:

1. Concrete failure due to aggregate presents a wide range of visible physical symptoms (progressive spalling, "D" lines cracking away from joints and cracks, etc.) that are observed in concrete from ages that may range from 2 to 40 years. The overall pattern of distress, once it begins, is similar—regardless of the type of carbonate aggregate used in the concrete.
2. A corollary to this is that there appear to be different kinds of deleterious rock types, each having an effect on the durability of concrete. The rate, amount, and kind of effect depend on the interaction with the rest of the components of the concrete system.

Petrographic study of deteriorated concrete indicates that it is carbonated, soft, contains calcium sulfaluminate, and that most of the original hydrated calcium silicate compounds appear to have been replaced by calcium carbonate. Concrete at the distressed margins of a slab is chemically and physically a different system than when it was poured.

These observations all indicate the necessity for more knowledge of what takes place in concrete as it ages before the role of coarse aggregate can be evaluated.

Research Approach

The main objective of this phase of research is to learn, if possible, what physical and chemical changes take place in concrete as it ages. Concretes made from the same aggregate but of different ages are the main basis of study. A chronological sequence of cores was taken from concrete highways with a good service record and containing the same coarse aggregate. Two sets of cores representing different ages have been taken from concrete made from Alden stone (pure limestone) and Dubuque stone (dolomite). Similar sets of cores have been taken from concretes with poor service records. A chronological series of cores has been taken from concretes containing LeGrand and Otis stone.

All the cores taken are stored and sampled in a CO_2-free environment. Intervals at 1, 3, and 5 in. from the top of each core are systematically sampled. The matrix and coarse aggregate are separated and analyzed separately.

The following investigations will be carried out in the study: (a) chemical analysis of matrix and coarse aggregate for principal oxides (this includes sodium, potassium, and sulfate contents); (b) X-ray diffraction investigation of the various constituents; (c) petrographic study of thin and polished sections of the concrete; and (d) standard engineering tests—compressive strength and sonic modulus of the cores.

The study is under way at present and all the cores have been taken. Techniques for chemical analyses of matrix and cores have been worked out and systematic analyses have already begun.

CONCLUSIONS

Expansion studies on Iowa rocks produced results similar in most respects to those obtained by others (1, 2, 3). Dedolomitization occurs, to some degree, in dolomite-bearing rocks regardless of whether they expand or contract. This bears out earlier work on compositional variations associated with carbonate reactions—dedolomitization occurs in a high pH environment providing there is access for solutions. The expanding rocks as a whole are argillaceous-appearing dolomitic limestones or calcitic dolomites with fairly high insoluble residues ($> 7\%$), fine-grained matrix textures and effective porosities less than 8 percent. Contracting rocks range in composition from pure (low insoluble residue) limestones or dolomites to argillaceous dolomitic types with effective porosities greater than 8 percent. Not enough evidence has been accumulated to postulate a causative mechanism for expansion, but the results to date indicate that in addition to the insoluble residue content, the physical properties of the rock—pore structure and texture—are probably an important factor. Contraction of most carbonate rocks appears to be a definite property which should not be neglected in future work.

Research on the effect of environment on silicification of carbonate rocks indicates that the method by which the reaction is induced controls the intensity of reaction and its overall nature.

A review of the problem of deleterious behavior of certain rocks in Iowa shows they can have a wide range of properties. Study of highway concretes indicates that aggregates are related to the service record and that the pattern of distress appears to be similar regardless of when deterioration commences. Research on the "aging" of highway concrete was undertaken to learn more about the concrete system in the hope that it will provide information on the role of carbonate aggregates.

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Alkali-Silica and Alkali-Carbonate Reactivity Of Some Aggregates from South Dakota, Kansas, and Missouri

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•THIS paper summarizes the two investigations concerning alkali-carbonate reactivity that have been completed at the Waterways Experiment Station. Additional investigations are in progress. These observations relate to aggregates from areas from which alkali-carbonate reaction had not been reported before this symposium. The first part describes an instance of the identification of brucite in dolomitic limestone affected by an alkali-carbonate reaction. The second part describes concrete from structures, in some of which an alkali-carbonate reaction has taken place with a limestone containing no dolomite that can be detected by X-ray diffraction. The paper raises more questions than it answers; if it stimulates additional investigation that does supply some additional answers, it will serve its purpose.

The investigations were concerned with aggregates from South Dakota, Kansas, and Missouri; the structures from which the concrete cores discussed in the second part were taken are all located in the northeastern quadrant of Kansas and the southeastern quadrant of Nebraska. For many years an increasing body of literature has stated that in part of Kansas, and in parts of other Great Plains states, there are problems relating to concrete durability that are unique. The term "sand-gravel aggregate" was coined to describe the predominant class of natural aggregates in the area. The term "cement-aggregate reaction" was coined to designate a phenomenon believed to be uniquely at work in contributing significantly to expansion and consequent damage to concrete in the area. During much of the period in which the literature on "cement-aggregate reaction" and "Kansas reactivity" was being developed, there were also developing both an improved understanding of the factors involved in the behavior of aggregates in concrete, and a conviction that physical and chemical mechanisms that control the behavior of aggregates in concrete apply generally throughout the world, whenever the participating factors and conditions come together. The ameliorative measure most widely and successfully used in combating "cement-aggregate reaction" in Kansas is the addition of some coarse aggregate to the sand-gravel aggregate concrete; this "sweetening" procedure has been believed to be most effective when the coarse aggregate added is a crushed carbonate rock.

SOUTH DAKOTA SAND

Background

In petrographic examination of sand from Watertown, South Dakota, and of mortar bars, and concrete cores containing this sand, the Corps of Engineers Missouri River Division Laboratory detected (1, 2) aggregate particles of types known to participate in alkali-silica reaction in concrete and reacted shale particles. Quick chemical tests made at MRDL on sands containing different amounts of shale particles like those that

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had reacted, indicated an apparent direct relation between amount of shale and amount of dissolved silica. Length-change measurements of mortar bars to determine alkali-aggregate reactivity, made with different amounts of shale particles in the sand, showed expansion not greater than 0.025 percent at one year with as-received sand, but abundant signs of reaction. As a consequence, the MRDL raised questions about alkali-aggregate reactivity of montmorillonitic shales, and suggested that montmorillonite might be a reactive mineral.

Samples

Seven mortar bars representing portions of two sets, made with high alkali cement, that had been tested to an age of one year for length change by method CRD-C 123-57 (3); a number of shale particles separated by flotation on a liquid with a specific gravity of 2.0, from another portion of the sample of sand that was used as aggregate in the mortar bars; and about 10 pounds of the sand were obtained from the MRDL for study. The shale was the principal constituent of the sand with a bulk specific gravity below 2.0.

Tests

The tests were undertaken to identify the reactive constituent or constituents of the shale, particularly to confirm or disprove the suggestion that montmorillonitic clay was the material reacting with alkalies in the case under study. The carbonate particles in the mortar bars were investigated because reaction rims, observed as color changes, were seen in some carbonate particles or in the surrounding mortar.

Several different reacted shale particles dissected from mortar bars were pulverized, mixed with water, air-dried on glass slides, and scanned on an X-ray diffractometer, using nickel-filtered copper radiation at 30 kv and 27 ma, air-dry, and after saturation with glycerol.

A single particle and a composite of several shale particles separated from the sand by flotation were prepared for X-ray examination by the same methods. Several whole and several pulverized shale particles were placed in a solution of 0.75N potassium hydroxide (equivalent to 3 percent sodium hydroxide) for three days, and then part of the sample was washed several times and dried on a glass slide. The rest of the sample was placed in a 1.5N potassium hydroxide solution (equivalent to 6 percent sodium hydroxide) for four days, and then washed and allowed to dry on glass slides. Samples from both treatments were examined by X-ray diffraction, air-dry and after glycerol saturation.

Two carbonate particles surrounded by a thin zone of light-colored mortar on broken surfaces of one mortar bar, and one carbonate particle, with a dark rim, on a broken surface of another bar were dissected out under a stereomicroscope, and the adhering mortar removed with a dissecting needle and forceps. Each separate carbonate grain was pulverized in water, the slurry was air-dried on a glass slide, and then scanned on the X-ray diffractometer.

About 50 carbonate rock grains were selected from sand retained on the No. 8 sieve in the sand sample, one-half by appearance and one-half by testing with dilute hydrochloric acid, as resembling the types which had developed reaction rims in the mortar bars. Portions of broken particles from each group were pulverized in water to produce composite slurries which were dried on glass slides, and X-ray patterns made of them. Saturated surface-dry weight and volume of the particles in each group were determined, and the specific gravity was calculated. Each group was then stored in 0.75N sodium hydroxide solution for almost 11 months. The particles were then washed, and the volume redetermined. Each group was examined with a stereomicroscope, pulverized in water to make a composite, dried on glass slides, and examined by X-ray diffraction. Twenty to thirty additional carbonate particles from the sand retained on No. 8 sieve were selected after examination with a stereomicroscope. They were divided into four groups; each group was pulverized and examined by X-ray diffraction as tightly packed powders.

TABLE 1

COMPOSITION OF SHALE PARTICLES DETERMINED BY X-RAY DIFFRACTION

Shale Particles	Relative Amounts of Constituents in Samples				
	Low Cristobalite-Tridymite	Quartz	Montmorillonite	Illite	Feldspar
Unreacted (portion of separated fraction added to mortar bars)	Major	Major	Major	Minor	Very minor
Reacted (found in mortar bars)	Not found	Major	Major	Major	Minor
Reacted experimentally (3 days in KOH solution)[1]	Minor	Major	Major	Major	Minor
Reacted experimentally (4 additional days in KOH solution)[2]	Not found	Major	Major	Major	Minor

[1] Part of same sample as that in line 1, after 3 days in KOH equivalent to 3% NaOH.
[2] Second part of same sample, after 4 more days in KOH equivalent to 6% NaOH.

Results

Alkali-Silica Reaction.—The gray and brown shale particles were tabular with rounded corners and edges. Broken surfaces of unreacted shale particles appeared to be ordinary shale and looked unlike broken surfaces of the reacted shale in the mortar bars. The reacted particles were easy to distinguish in the mortar bars because they exhibited thin, hard peripheral shells with radial cracks, and soft, moist centers shrunken away from the shells, and gel-filled voids were common at or near the surfaces of the shale particles. The composition of the unreacted shale and the reacted particles in the mortar bars differed (Table 1). The unreacted particles contained a large amount of opal of the type described from Kansas by Swineford and Franks (4) as low cristobalite-tridymite (SiO_2) with a large amount of quartz (SiO_2) and minor montmorillonitic clay, clay-mica (illite), and feldspar. There was no evidence of low cristobalite-tridymite opal in the reacted particles. Any form or combination of cristobalite or tridymite is readily soluble in alkaline solutions and capable of producing alkali-silica reaction in concrete.

The (001) basal spacing of the montmorillonite in the reacted particles, air-dry and glycerol-saturated, measured about 12A and 14A, respectively, while the basal spacings of the montmorillonite in the unreacted particles measured about 15A and 18A, air-dry and glycerol-saturated, respectively.

X-ray examinations of unreacted shale after two intervals of storage in potassium hydroxide solution showed progressive decrease and eventual disappearance of the low cristobalite-tridymite peaks and a change in the (001) basal spacing of the air-dry and glycerol-saturated montmorillonitic clay from about 15A and 18A, to about 12A and 14A, which are the values found in potassium-bearing montmorillonitic clay (5). The changes indicated that all of the low cristobalite-tridymite dissolved, and that the potassium ions of the solution replaced the exchangeable cations naturally present in the clay.

The experimental results explained the differences between reacted and unreacted shale particles, and also the shale-mortar reaction in the mortar bars. The low cristobalite-tridymite opal, not the montmorillonite, was the apparent source of the reactive silica in the alkali-silica reaction. If the montmorillonitic clay in the shale had contained exchangeable sodium or potassium, and the cement had been low in alkali, cation exchange between shale and paste might have displaced the alkalies in the clay by calcium, releasing alkali ions. However, the cation exchange that actually occurred removed alkalies from availability to participate in alkali-silica reaction.

TABLE 2

COMPOSITION OF CARBONATE PARTICLES IN SANDS FROM VICINITY OF WATERTOWN, SOUTH DAKOTA, AS DETERMINED BY X-RAY ANALYSIS

Samples	Relative Amounts of Constituents in Particles				
	Dolomite	Calcite	Brucite	Quartz	Feldspar
Particles with reaction rims in mortar bars:					
Piece A	Major	Major (dol.)	Minor	—	—
Piece B	Major	Minor	Very minor	Trace	—
Piece C	Major	Minor	Very minor	—	—
Particles in sand:					
Natural state[1]	Major	Major to none	—	Trace	Trace
After 11 months in 3% NaOH solution[2]	Major	Minor	Minor (cal.)	Trace	Trace

[1] Results are an average of six patterns; two represent samples before immersion in sodium hydroxide and four are general samples selected to show composition.

[2] Results are for group selected by appearance and by acid testing.

TABLE 3

PHYSICAL DATA[1] FOR CARBONATE ROCK PARTICLES FROM WATERTOWN, SOUTH DAKOTA, SAND USED IN MORTAR BARS

Dolomite or Dolomitic Limestone Particles Retained on No. 8 Sieve	Natural State			After 11 Months in 3% NaOH Solution	
	Weight (g)	Specific Gravity[2]	Volume (ml)	Volume (ml)	Volume Increase (%)
22 particles selected by appearance	1.54	2.80	0.55	0.60	9.1
26 particles selected by acid testing	2.06	2.94[3]	0.70	0.75	7.1

[1] Measured while particles were saturated surface-dry.

[2] Specific gravity of pure dolomite is 2.85 ± 0.01; that of pure calcite is 2.71.

[3] Probably acid testing developed small pits on surfaces of particles and surface water was not completely removed from these pits when an effort was made to bring the particles to saturated surface-dry condition. Therefore this value, calculated from measured weight and volume determined by displacement (2.06/0.70 = 2.94), is higher than it should be.

Alkali-Carbonate Reaction.—Some of the white chalky carbonate particles on broken surfaces of the mortar bars had dark rims or were bordered by a thin band of light-colored mortar. X-ray examination of three of the particles (Table 2) revealed that each was composed of dolomite, calcite, and brucite ($Mg(OH)_2$) in that order of abundance. The amount of brucite was small, but it was definitely present. Because brucite is an improbable constituent of a dolomitic limestone, this composition indicated that some of the dolomite had altered to brucite in the mortar bars; this is the dedolomitization reaction previously reported in concrete (6, 7). The composition of similar carbonate particles in their natural state was determined to see if such particles would produce brucite in an alkaline solution, and to see if the reaction would produce in sand-sized grains expansions detectable by a simple physical test. Carbonate rock particles from the sizes coarser than the No. 8 sieve in the sample from the source of the sand used in the mortar bars were selected to resemble those with reaction rims in the mortar bars (Table 3). Most of the particles had spots of the manganese oxides ("wad") scattered over their surfaces, and some were stained with iron oxides. The particles in the group selected by appearance and in the group selected by acid testing were divided into three lithologic varieties based on grain size, wad coatings, and iron-oxide coatings. The varieties were not successfully distinguished after storage in sodium hydroxide solution for 11 months because of bleaching and chemical changes. For this reason, all of the particles in each group were pulverized into a composite sample after measurement of volume and before X-ray examination. The particles as received varied in composition from dolomite to dolomitic limestone with traces of quartz and feldspar (Table 2). There was no detectable brucite. X-ray examination of the samples after storage for 11 months in 0.75N sodium hydroxide solution showed that some of the dolomite had been altered to calcite and brucite; much less new brucite was apparent than new calcite. (The apparent difference in quantity may result from the low linear absorption coefficient for copper radiation of magnesium hydroxide as compared with calcium carbonate.) Measurements of the particles before and after the 11 months storage in alkaline solution showed a detectable increase in volume.

Conclusions

Alkali-Aggregate Reaction.—The shale particles had participated in alkali-silica reaction, and X-ray diffraction examination of reacted shale particles from the mortar bars and of shale particles from the sand not used in mortar bars showed differences. The unreacted particles contained a large amount of low cristobalite-tridymite opal (4) which was missing in the reacted particles. Any kind of opal can participate in alkali-silica reaction in concrete. Both unreacted and reacted shale contained some montmorillonitic clay, but the clays in the two conditions differed in basal spacing. The reason for this difference was shown to be cation exchange in which divalent cations in the clay (probably Ca and Mg) were replaced by potassium ions from the cement. Thus, the source of reactive silica in the shale particles was apparently low cristobalite-tridymite opal and there was no evidence that montmorillonitic clay participated in alkali-silica reaction in portland cement concrete.

Carbonate Rock Reaction.—Rims consisting of dark borders in the carbonate rock or of thin bands of light-colored mortar surrounding the carbonate rock were observed around carbonate particles on broken surfaces of the mortar bars. The carbonate rocks contained dolomite, calcite, and a small amount of brucite ($Mg(OH)_2$). X-ray analysis of selected carbonate particles from the sand used in making the mortar bars showed them to be dolomite or dolomitic limestone with small amounts of quartz and feldspar; no brucite was found. The volume, weight, and specific gravity of some of the carbonate particles from the sand were determined; two groups of these particles were then placed in 3 percent sodium hydroxide solution for 11 months, and their volume and mineralogical composition were again determined. The volume of the groups had increased from 7.1 to 9.1 percent; some of the dolomite had been converted to calcite and brucite by dedolomitization. The absence of brucite in carbonate particles in their natural state, its presence in particles with reaction rims in mortar bars, and the presence of brucite plus the volume change of the carbonate particles after storage in sodium hydroxide solution for 11 months all indicate that some dedolomitization (6, 7) had occurred in the mortar bars, and that the reaction rims, in this case, were observable evidence of this reaction. This is believed to be the first time that carbonate rock reaction has been reported in Corps of Engineers specimens, and the first instance in which brucite has been directly identified among the products of alkali-carbonate reaction in concrete or mortar.

AGGREGATES FROM KANSAS AND MISSOURI

Background

In 1960, representatives of the Waterways Experiment Station and of other agencies concerned with research on the behavior of aggregates in concrete held discussions on the investigational attack required to elucidate the mechanisms involved in "cement-aggregate reaction" as manifested by "sand-gravel aggregates," typically in Kansas.

At about this same time representatives of the Kansas City District and the Missouri River Division (MRD) Offices of the Corps of Engineers were making aggregate investigations for Milford Dam, proposed for construction on the Republican River near Milford, Kansas. As has been the case in all serious considerations of aggregate suitability and of anticipated concrete performance in Kansas in the last several decades, it was difficult to establish a rational basis for selecting aggregates that might be used with confidence that the concrete structures in which they were employed would provide the desired service. These difficulties arise primarily from a lack of knowledge of the factors that contribute to poor performance of concrete in the area, because no fundamental investigational work has been done on the problem.

During the aggregate investigation for Milford Dam, representatives of the District and the MRD made several trips to examine structures, on one of which they were joined by a representative of the Office, Chief of Engineers, and by one of the authors of this paper.

The aggregate investigation for Milford Dam has already shown that the Towanda limestone, quarried near the Milford Dam site, was physically superior to most coarse aggregate from sources economically available. The principal question remaining was whether it would be advisable to list the sands produced from the Republican River and the section of the Kansas River just east of the confluence of the Republican River and the Smoky Hill River among the approved sources of fine aggregate. The answer was not readily apparent, because these sands make up the bulk of the product known as sand-gravel aggregate, and because aggregates from the particular reaches of the Republican River under consideration include some of those which have been associated with "cement-aggregate reaction."

The examinations of structures and the aggregate tests that had been made did not provide conclusive answers, and thus the WES representative suggested that four cores be taken, three from structures examined during the inspection trip and one additional core from a 10- to 15-yr-old concrete structure containing sand from the Republican River or the Kansas River at Junction City, and limestone coarse aggregate. Examination of these cores was expected to provide additional evidence helpful in reaching a decision on whether or not to include Republican River sand, and Kansas River sand from the region just downstream of the confluence of the Republican and Smoky Hill Rivers, among the approved sources of fine aggregate.

Samples

Eight 6-in.-diameter diamond-drilled concrete cores from structures in Kansas and Nebraska were received late in 1961 or early in 1962. All contained crushed limestone coarse and sand-gravel or natural fine aggregate. Information on the structures and materials is given in Table 4.

Tests

Each core was examined when received to determine its general condition, whether old cracks were present, whether any chemical reactions after drilling were indicated by deposits on the drilled surface, and whether there was any evidence of freezing and thawing, sulfate attack, alkali-silica reaction or any other reaction between aggregate and cement paste. After the preliminary examination, each core was placed in a separate container and covered with water to let the dry concrete regain moisture and to determine whether soaking at room temperature would produce any signs of reaction not present in the concrete as received. After one or more days of soaking, each core was re-examined to find whether any changes had taken place, and one or more surfaces were sawed and examined for evidences of alkali-silica reaction that had taken place before drilling. After this examination the sawed surfaces were scrubbed with acetone to remove cutting oil, and the pieces of the core were soaked and re-examined after one to three days to determine whether any sign of the progress of alkali-silica reaction was developing.

Where cores KC-1, -4, and -5 were examined, rims of different color from the rest of the piece could be seen just inside the boundaries of many of the pieces of car-

TABLE 4

AGE, LOCATION OF STRUCTURE, COMPOSITION OF CORES, AND MEAN ANNUAL RAINFALL FOR COUNTY OF LOCATION

Specimen	Date Placed; Age (yr)	Structure and Location	Horiz. or Vert. Core	Aggregate and Source		Mean Annual Rainfall (in.)
				Coarse	Fine	
KC-8	1918 43	World War I sewage plant, now swimming pool, Camp Funsten, Ft. Riley, Kan.	V	1-in. maximum limestone	Republican or Kansas River near Junction City, Kan.(?)	31.8
KC-1	1924 37	Abandoned highway pavement, Scandia, Kan.	V	2½-in. maximum crusher-run limestone; National Stone quarry, Louisville, Nebraska(?)[1]	Republican River, Clay Center, Kan.(?)	25.9
KC-9	1927 34	Right abutment of highway bridge, Clark's Creek, Geary County, Kan.	H	2½-in. maximum crusher-run limestone, Cottonwood formation(?)	Republican River, Clay Center, Kan.(?)	31.8
KC-7	1945 16	Swimming pool, officers' club Ft. Riley, Kan.	H	1-in. maximum crushed limestone	Republican River, More Sand Co., Junction City, Kan.	31.8
KC-6	1947 14	West wall of garage, Harlan County Dam, Neb.	H	1-in. maximum crushed limestone, Loring quarries, Bonner Springs, Kan.	Republican River, More Sand Co., Junction City, Kan.	20.9
KC-4 KC-5	1949 12	Building, Harlan County Dam, Neb.	H	1-in. maximum crushed limestone, Pixley Mine, Independence, Mo.	Kansas River, Turner, Kan.	20.9
KC-11	1955 6	North wall, compressor room, boiler plant, hospital, Ft. Riley, Kan.	H	1-in. maximum crushed limestone, Towanda formation, Milford, Kan.	Republican River, More Sand Co., Junction City, Kan.	31.8

[1] It has also been suggested that the aggregate came from the old Kerford quarry.

bonate coarse aggregate. In KC-1 there were also partial rims, or projecting lobes, in the paste next to parts of the edges of some of the carbonate coarse aggregate. These rims suggested that the reactions between carbonate coarse aggregates and alkalies in portland cement might have taken place in these concretes. These reactions include dedolomitization, described by Hadley (6), and the rim formation discussed in several publications by John Lemish and various coworkers (8-13). Therefore, parts of the rims in the aggregate particles, the centers of rimmed particles, and parts of the cement paste immediately bordering rimmed carbonate rocks were dissected out and examined by X-ray diffraction to see whether the reported compositions and reaction products of dedolomitization were present. Slices of each core containing carbonate aggregate were etched with hydrochloric acid by the procedure described by Lemish et al. (9) or in 10 percent acetic acid solution. A sample of limestone from the source of the coarse aggregate used in cores KC-4 and -5 was examined by stereomicroscope and by X-ray diffraction to see whether it was similar to the stone in those cores. Cracks, the kind of aggregate with which they were associated, carbonate coarse aggregate with and without rims, and chert or cherty limestone were counted on sawed slices of several cores.

Pieces of each variety of carbonate rock in the cores were selected after the outer surfaces, sawed slices, and etched slices of the cores had been examined. The color of each variety was named by comparison with the Rock-Color Chart (14). The rock was broken out of the concrete and freed of mortar, ground, and examined by X-ray diffraction. The crushed coarse aggregate in cores KC-7, -8, and -9 contained chert or cherty limestone that had developed rims and, in some cases, internal cracks. The reacted chert was sampled and examined by X-ray diffraction, and in immersion liquids to determine whether any chalcedonic silica, with indices of refraction below the lower index of quartz, was present.

A sample of mortar was taken from each core, away from coarse aggregate, examined under the stereomicroscope to be sure that no coarse aggregate was included, and was then crushed and sieved over the No. 100 sieve. This procedure concentrates fine aggregate in the fraction retained on the sieve and cement paste in the fraction passing the sieve. Each fraction was ground to pass the No. 325 sieve, packed in a sample holder so as to minimize preferred orientation, and examined by X-ray diffraction.

Thin section blanks, chosen from interesting areas of each core, were impregnated under vacuum with an epoxy resin formulation, mounted with epoxy resin, and prepared for microscopical examination. Thin sections prepared several years ago from cores from the McPherson test road (15), which contained Republican River sand-gravel from Wakefield, Kansas, with each of two cements with and without the addition of 30 percent crushed Moline limestone, were re-examined for comparison.

Because the cores were conspicuously dry when received, although they had presumably been drilled with water and some had reached the laboratory within a few days after drilling, it appeared desirable to determine whether the concretes were potentially capable of expansion if they were exposed to water or high humidity. Two prisms approximately 4 in. by $1\frac{1}{2}$ in. by $1\frac{1}{2}$ in. were cut from each core, except KC-7 and KC-9, and a ball bearing cemented to the center of each end face of each prism with an epoxy resin to provide a reference point. After the resin had hardened at room temperature for several days, one prism from each core was stored over distilled water in an individual polyethylene container, and the other prism was stored in another individual polyethylene container and covered with distilled water to a depth of $1\frac{1}{2}$ in. The containers had tight-fitting lids, and a piece of heavy polyethylene large enough to overlap each side of the container at the top was laid over the opening before the lid was pressed down. The humidity in the container reached a level high enough for moisture to condense on the underside of the polyethylene sheet if an inch of water were placed in the bottom of the container.

Each prism was equilibrated for 72 hr at room temperature, and its reference length then measured with a micrometer graduated to 0.0001 in. The prisms stored above water were measured at 28-day intervals, at room temperatures ranging from 23.0 to 27.1 C. The other prisms were subjected to a cycle like that of ASTM Designation:

TABLE 5

CONSTITUENTS OF THE MORTAR FRACTION IDENTIFIED BY X-RAY DIFFRACTION

Constituent	Cores															
	Finer than No. 100 Sieve								Coarser than No. 100 Sieve							
	KC-1	KC-4	KC-5	KC-6	KC-7	KC-8[1]	KC-9	KC-11	KC-1	KC-4[2]	KC-5[2]	KC-6[3]	KC-7[4]	KC-8[5]	KC-9	KC-11
Sulfoaluminate																
$32H_2O$	3	—	tr	tr	—	—	tr	tr	tr	tr	tr	tr	—	—	tr	tr
$11H_2O$	—	—	—	—	—	—	tr?	—	—	—	—	tr	—	—	—	—
C_4AH_X	—	—	—	—	?	—	—	—	—	—	—	—	tr	—	—	—
Monocarboaluminate	tr	3	3-	3	3+	3+	3+	3-	—	tr	tr	tr	tr	tr+	3	—
Hydrogarnet	tr	tr	tr	tr	—	tr	tr	?	tr	—	—	—	—	tr	—	—
$Ca(OH)_2$	3	3	2	3	2	3	2	2	3	3-	3-	3-	3	3	3-	tr
Calcium silicate hydrate	Present in all samples; most lines overlapped by others								pr	pr-	pr	pr	pr	pr	pr	pr
Residual unhydrated cement	Traces probably present in all samples								tr	tr-	tr	tr	tr	?	?	pr
Quartz	Most prominent constituent of all samples; probably less abundant than the sum of the feldspars if the whole mortar is considered								1	1	1	1	1	1	1	1
									Most prominent constituent of all of the concretes							
Feldspar	More potassium than plagioclase feldspar, except in KC-5, and -6								1-	3	1	2	2	2+	2	2
	1	1	3	2	1	1	3	1								
Calcite	3	2	1	2	tr	2	2	3+	3	3	3	3	3	2	3	3

[1] Extra line at 10.1 A.
[2] Extra line at 9.2 A.
[3] Extra line at 10.2 A.
[4] Extra line at 10.4 A.
[5] The metastable calcium aluminate, $2CaO \cdot Al_2O_3 \cdot 8H_2O$, is also present, and minor mica.

Note: 1 = major; 2 = moderate; 3 = minor; tr = trace; pr = present; ? probably present. KC-2, -3, -10 sand-gravel concretes; others contain carbonate coarse aggregates. The calcite in the sand-gravel concretes represents both occasional calcareous grains in fine aggregate and secondary calcite.

TABLE 6

LENGTH CHANGE OF SAWED CONCRETE PRISMS STORED IN SEALED CONTAINERS OVER WATER

Specimen	Reference Length After 4 Days in Water (in.)	Length Change (%)												
		32 Days	60 Days	88 Days	116 Days	144 Days	172[1] Days	200 Days	228 Days	256 Days	284 Days	312 Days	340 Days	368 Days
KC-1	4.4585	+0.034	+0.054	+0.074	+0.074	+0.074	+0.070	+0.065	+0.061	+0.061	+0.053	+0.051	+0.049	+0.063
KC-4	4.5615	+0.022	+0.044	+0.063	+0.059	+0.061	+0.057	+0.059	+0.055	+0.061	+0.053	+0.050	+0.053	+0.066
KC-5	4.7485	+0.038	+0.057	+0.067	+0.067	+0.063	+0.072	+0.074	+0.069	+0.074	+0.074	+0.078	+0.082	+0.099
KC-6	4.5085	+0.029	+0.051	+0.058	+0.062	+0.060	+0.060	+0.058	+0.055	+0.064	+0.055	+0.055	+0.058	+0.067
KC-8	4.4977	+0.022	+0.044	+0.071	+0.064	+0.064	+0.056	+0.062	Not read	+0.064	+0.078	+0.100	+0.098	+0.076
KC-11	4.4698	+0.022	+0.060	+0.092	+0.081	+0.078	+0.056	+0.065	Not read	+0.065	+0.072	+0.087	+0.098	+0.081

[1] Water in all containers changed after 172 days.

Note: Air temperature in storage room ranged from 26.7 to 23 C; temperatures of water equilibrated with the room ranged from 26.4 to 22.1 C.

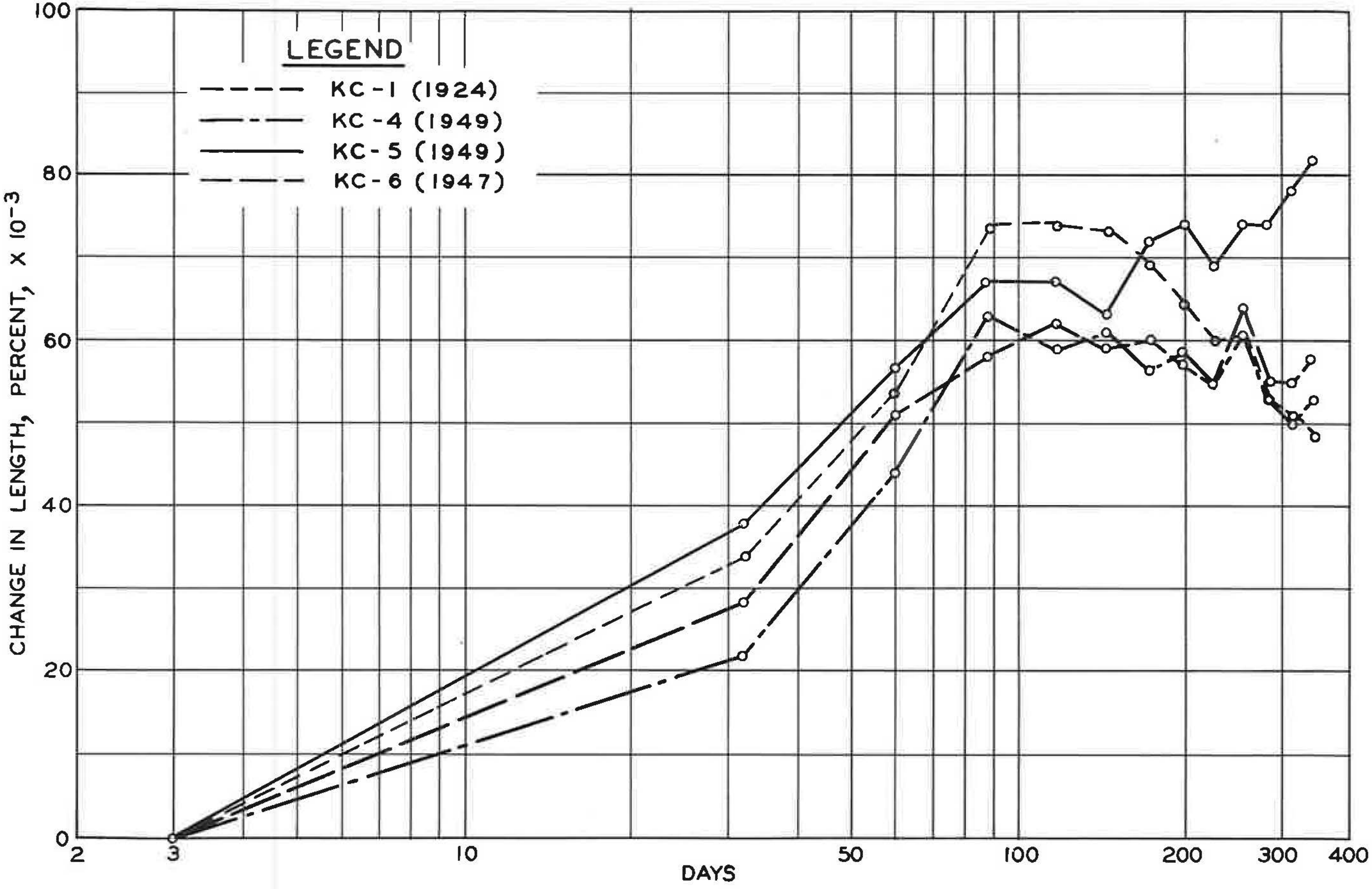


Figure 1. Expansion, during storage over water at 25± 2 C, of sawed concrete prisms from a pavement at Scandia (KC-1) and from office building and garage at Harlan County Dam.

TABLE 7

LENGTH CHANGE OF SAWED CONCRETE PRISMS SUBJECTED TO A CONROW CYCLE

Specimen	Reference Length After 4 Days in Water (in.)	Length Change (%) After: Stored in Water, 29 Days at Room Temp.	Length Change (%) After: Stored in Water, 7 Days at 55 C	Length Change (%) After: Stored in Air, 7 Days at 55 C	Length Change (%) After Designated Time[1] in Water at Room Temperature: 1 Day	7 Days	28 Days	56 Days	84 Days	112 Days	140 Days	168 Days	196 Days	224 Days	252 Days	280 Days	308 Days
KC-1	4.4170	+0.020	+0.057	-0.041	-0.025	0	+0.032	+0.032	+0.038	+0.059	+0.041	+0.038	+0.027	+0.027	+0.032	+0.029	+0.034
KC-4	4.5725	+0.028	+0.136[2]	-0.015	+0.004	+0.024	+0.085	+0.112	+0.048	+0.050	+0.057	+0.061	+0.076[3]	+0.061	+0.051	+0.061	+0.079
KC-5	4.7290	+0.027	+0.027	-0.057	-0.025	-0.006	+0.038	+0.051	+0.044	+0.051	+0.053	+0.046	+0.049	+0.051	+0.046	+0.051	+0.061
KC-6	4.5485	+0.040	+0.057	-0.033	-0.004	+0.009	+0.042	+0.055	+0.053	+0.059	+0.059	+0.053	+0.051	+0.057	+0.059	+0.057	+0.015[4]
KC-8[5]	4.5303	+0.033	+0.108	-0.035	+0.004	+0.042	+0.132	+0.132	+0.132	+0.146	+0.148	+0.161	+0.159	+0.159	+0.166	+0.172	+0.168
KC-11[5]	4.4753	+0.036	+0.159	+0.009	+0.036	+0.087	+0.217	+0.230	+0.230	+0.237	+0.239	+0.239	+0.239	+0.241	+0.244	+0.241	+0.241

[1] First day in water at room temperature is 54th day since start of test; water in all containers changed after 112 days.

[2] Ball bearing fell out, was replaced; later readings may not be significant.

[3] High reading was checked several times. Reason for high reading unknown.

[4] Rust deposit on ball bearing, was scratched off, left pit in bearing; reading is not valid.

[5] Tests of these prisms started at later date than first six.

Note: Air temperature in the storage room ranged from 26.2 to 22.9 C; temperatures of water equilibrated with the room ranged from 26.4 to 22.4 C.

C 342-61T (Potential Volume Change of Cement-Aggregate Combinations, the Conrow Test) (16, 17), except that the temperature range of the room in which the containers were stored was greater than that permitted in the test procedure.

Results

Table 5 contains the results of X-ray examinations of the cement paste concentrates. Table 6 and Figures 1 and 2 show the length-changes of concrete prisms exposed at high humidity, and Table 7 and Figures 3, 4 and 5 show the length changes of prisms exposed to a Conrow cycle. All of the descriptions of carbonate coarse aggregates from the cores are grouped in Table 8.

KC-1.—The sample was an unreinforced vertical core $8^3/_8$ in. long from an abandoned highway pavement at Scandia, Kan., placed about 1924. The coarse aggregate was very pale orange to dark yellowish-brown, somewhat shaly limestone (Table 8), apparently crusher-run stone ranging from $2^1/_2$-in. maximum size to passing the No. 4 sieve. The high proportion of sand retained on the No. 50 and No. 100 sieve suggested that the fine aggregate had been used in the grading in which it had been obtained. The source of the cement is not known. The paste was grayish in most of the concrete; the mortar was well consolidated with a few irregular voids up to $^3/_8$ in. in maximum dimension. A few small pockets of white opaque gel were found, and two fresh gel spots developed on the surface of one piece of the core after several days of soaking. The finished surface was weathered, and worn so that the sand grains stood in relief above the paste. The core showed a few short cracks, believed to be old because the paste bordering them differed in color from the rest. A deposit that was relatively resistant to hydrochloric acid formed an irregular layer just below the pavement surfaces.

Carbonate coarse aggregate and associated reactions.—Some of the pieces of coarse aggregate had darker shells at the outer border next to the mortar. When pieces of the concrete were broken, the darker shells stuck to the mortar and the paler centers fell out. Some dark-shelled pieces of coarse aggregate were bordered by brownish lobes or tongues of mortar,

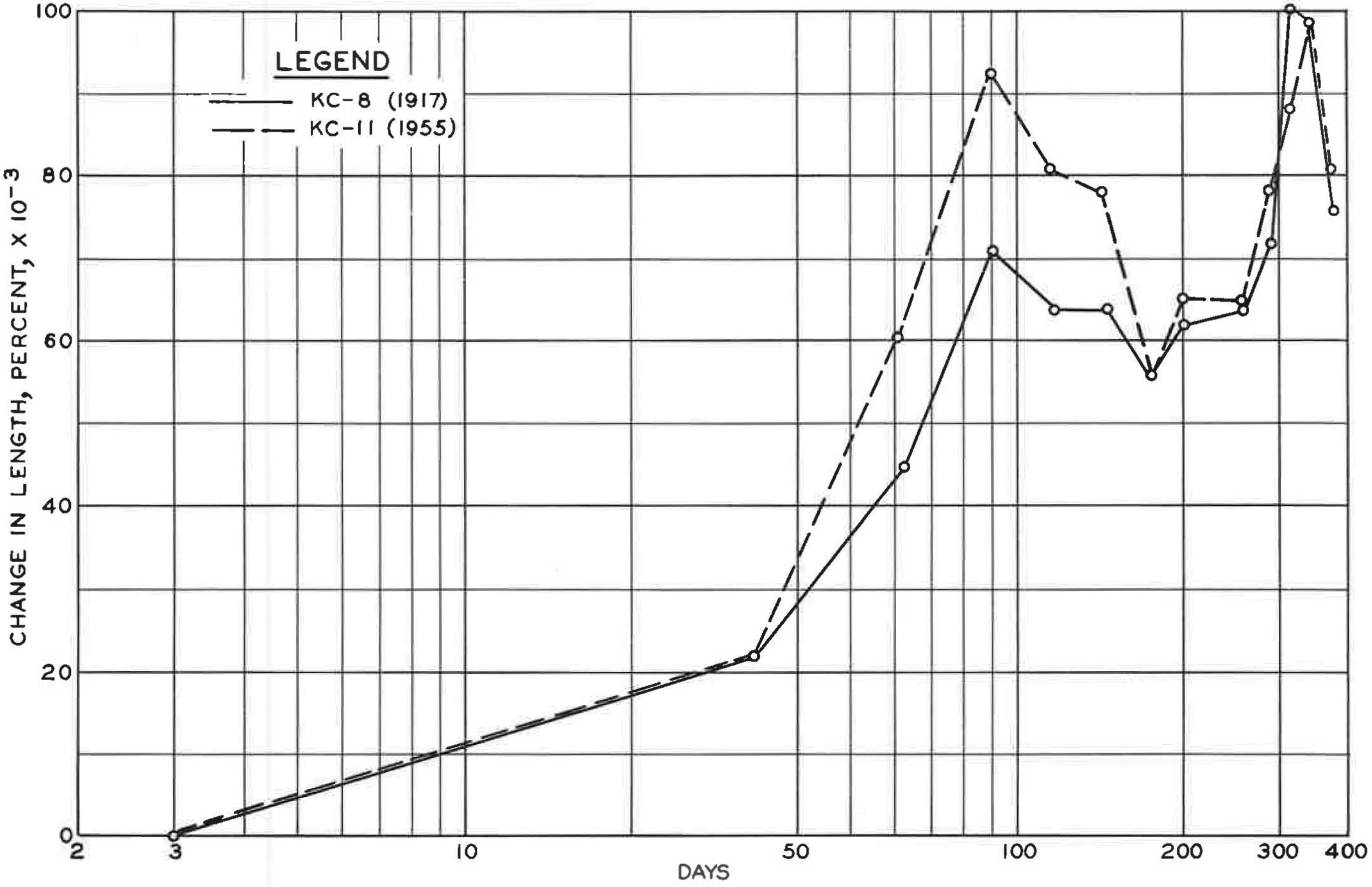
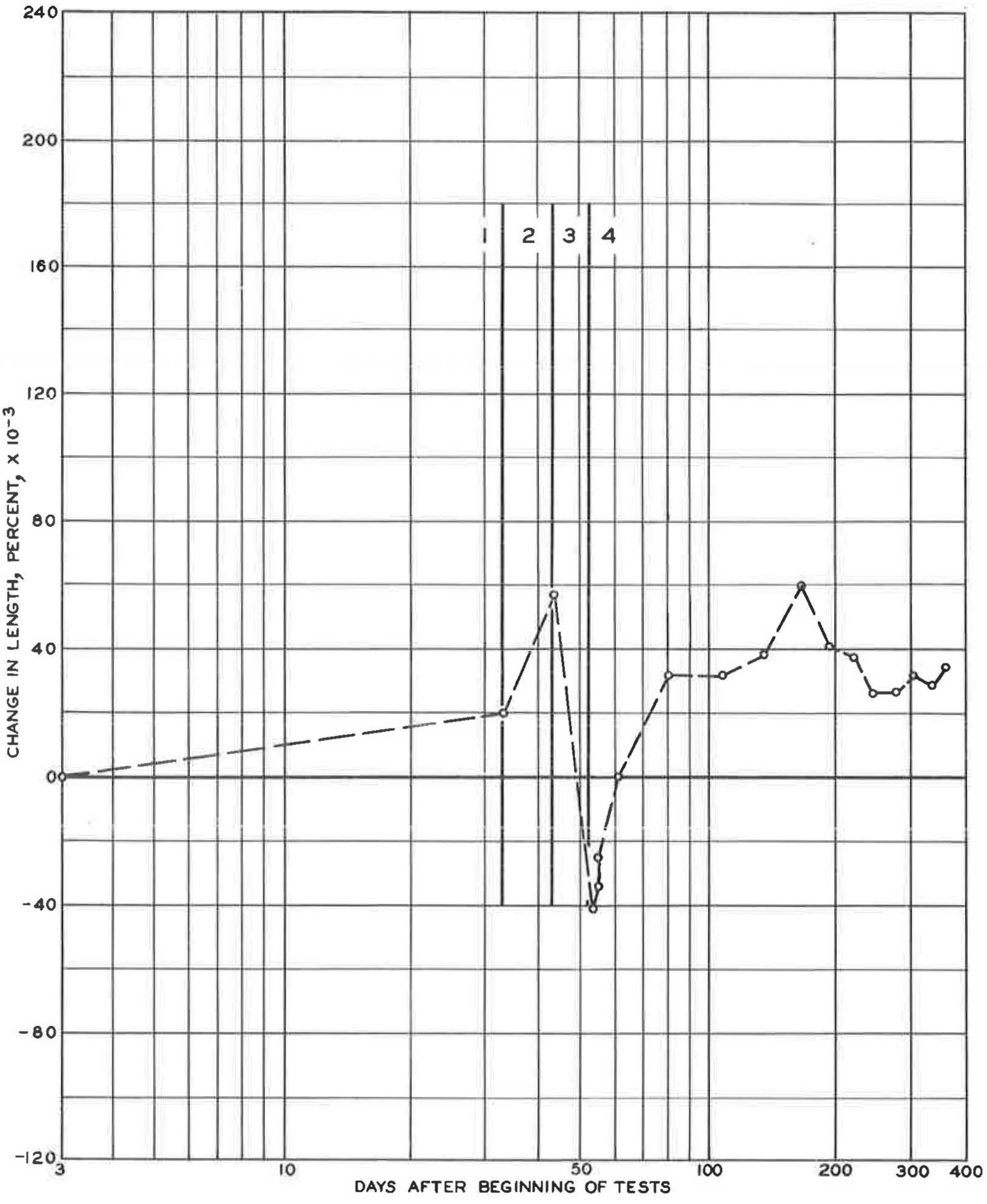


Figure 2. Expansion, during storage over water at 25± 2 C, of sawed concrete prisms from two structures at Fort Riley, Kan.

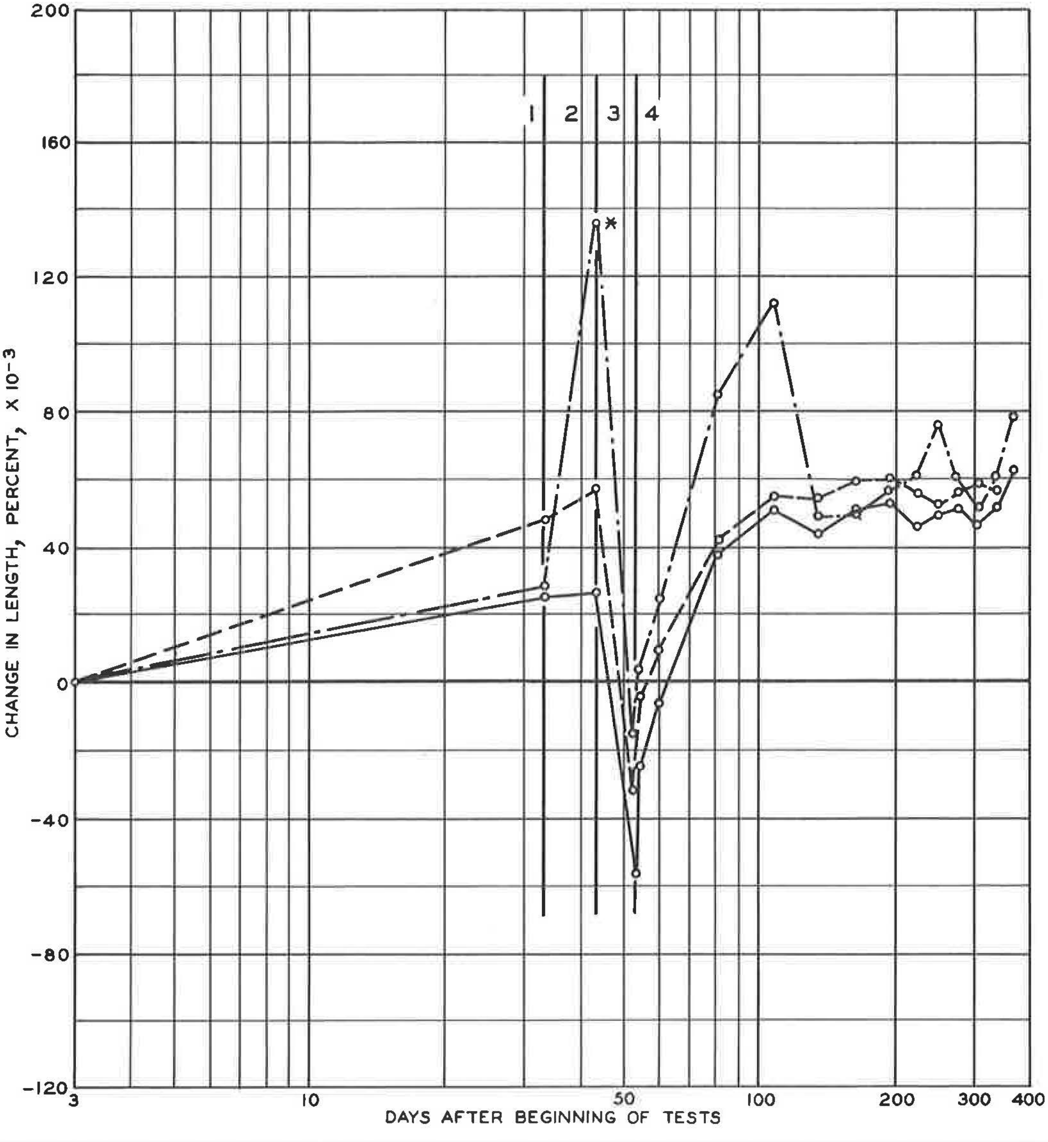


LEGEND

— — — KC-1 (1924)

1 = 33 DAYS IN WATER AT ≈ 23° C
2 = 7 DAYS IN WATER AT 55° C
3 = 7 DAYS IN AIR AT 55° C
4 = IN WATER AT ≈ 23° C

Figure 3. Effect of Conrow cycle on sawed concrete prisms from a structure at Scandia, Kan.



LEGEND

—·— KC-4 (1949)

——— KC-5 (1949)

— — — KC-6 (1947)

1=33 DAYS IN H_2O AT≈23° C

2=7 DAYS IN H_2O AT 55° C

3=7 DAYS IN AIR AT 55° C

4=IN H_2O AT≈ 23° C

NOTE: * BALL BEARING FELL OUT AND WAS REPLACED, LATER MEASUREMENTS MAY BE MEANINGLESS.

Figure 4. Effect of Conrow cycle on sawed concrete prisms from Harlan County Dam, Neb.

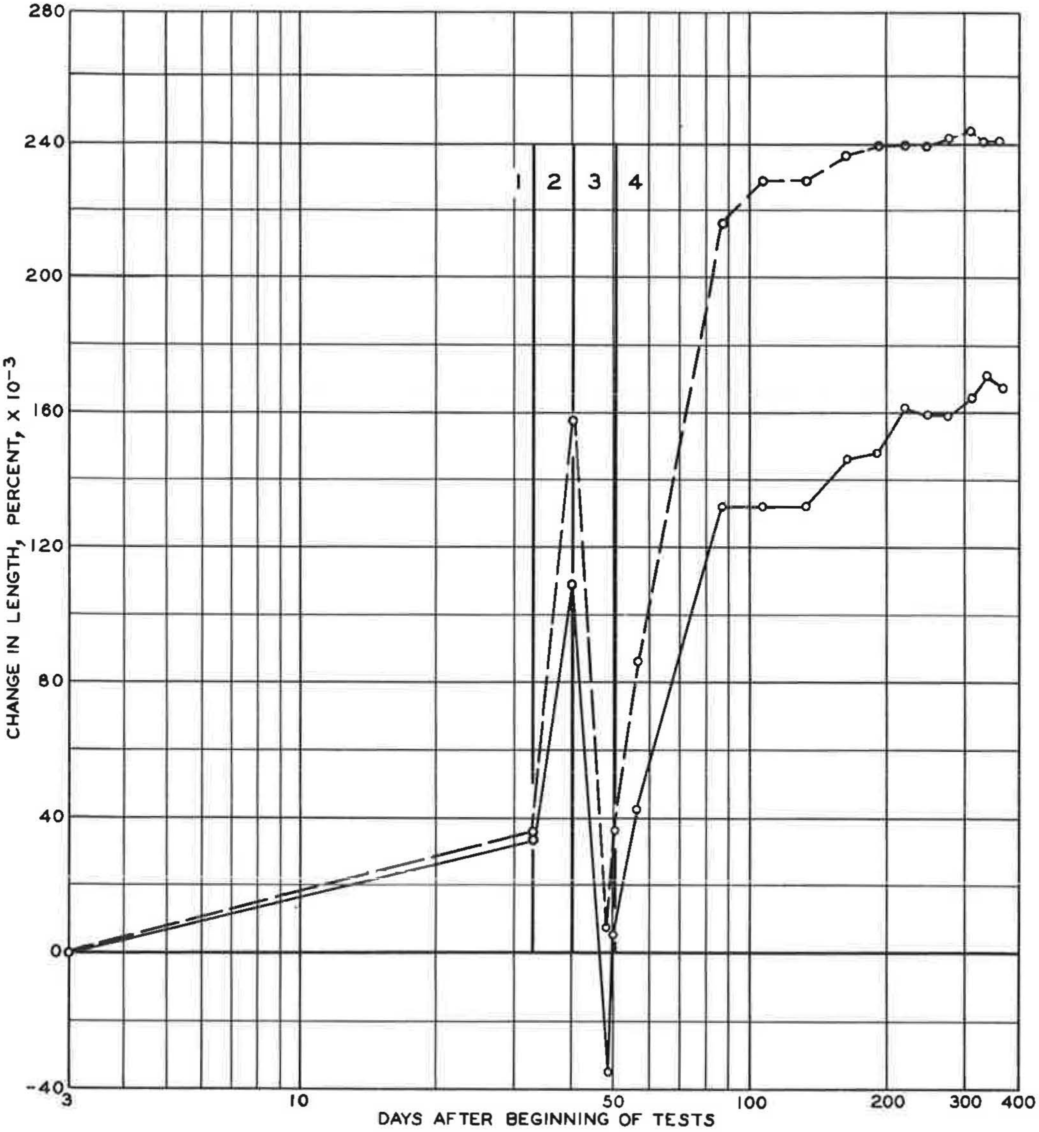


Figure 5. Effect of Conrow cycle on sawed concrete prisms from two structures at Fort Riley, Kan.

TABLE 8

COMPOSITION OF CARBONATE COARSE AGGREGATES IN EIGHT CONCRETE CORES

Specimen	Variety	Approximate Percent of Coarse Aggregate	Constituents Identified by X-ray
KC-1	Very pale orange (5YR 7/2) to pale yellowish-brown (10YR 7/2) fine-grained occasionally fossiliferous limestone, with slight tendency to form rims	75	Almost all calcite, minor chert, traces of kaolin-group clay and feldspar. (Chert is chalcedonic.)
	Moderate yellowish-brown to dark yellowish-brown (10YR 5/4 to 10YR 4/2) thin-bedded fossiliferous limestone with shale partings; fossils are coarse calcite and matrix is fine grained. Rims fairly prominent	15	Calcite major; chert minor; ferroan dolomite minor; kaolin-group clay; clay-mica, feldspar, pyrite in traces. (Chert is chalcedonic.)
	Pale yellowish-brown to dark yellowish-orange (10YR 6/2—10YR 6/6) limestone, a more weathered softer variety of that described just above. Rims fairly prominent	10	Constituents and proportions like those of previous variety
KC-4 and KC-5	Light olive-gray (5Y 6/1) ranging to medium light gray (N6) fine-grained limestone makes up almost all of the aggregate. Rims were common on etched surfaces. Traces of shaly and fossiliferous varieties were seen; no X-ray examinations of these were made.	97+	Major calcite; quartz very minor or traces; traces of clay-mica and other clay; no dolomite. Pattern of limestone from permanent sample previously tested was almost identical.
KC-6	Pale yellowish-brown (10YR 6/2) to light olive-gray (5Y 6/1) fine-grained dense limestone, some with faint rims	65	Major calcite; chert very minor to trace; dolomite, trace; traces of feldspar, clay-mica, chlorite, kaolin-group clay (?), pyrite
	Light gray (N7) fine-grained calcareous dolomitic sandstones to sandy limestones, which looked very much alike but showed the range in composition noted.	20	Major to moderate amounts of calcite and disseminated chert in all, with dolomite ranging from major to very minor; traces of clay-mica, feldspar, pyrite, chlorite, kaolin-group clay
	Somewhat weathered pale yellowish-orange shaly limestone (10YR 8/6)	5	Major calcite; moderate to minor chert; minor dolomite, very minor feldspar; clay-mica, very minor; traces of chlorite
	Light gray (N7) to medium light gray (N6) chert	10	Chert with very minor calcite, traces of dolomite and clay-mica
KC-7	Pale yellowish-brown (10YR 6/2) to yellowish-gray (5Y 8/1) dense fine-grained limestone, forming rims less soluble than interiors of pieces	50	Major calcite, minor chert, very minor dolomite; trace clay-mica
	Yellowish-gray (5Y 8/1) to light olive-gray (5Y 6/1) calcareous dolomitic cherts to cherty calcitic dolomites	30	All contain calcite, dolomite, quartz, in amounts ranging from moderate to major from piece to piece, with traces of feldspar, clay-mica, clays
	Pale yellowish-orange (10YR 8/6) to grayish-orange (10YR 7/4) weathered limestones and dolomites	15	Not examined
	Light gray (N7) chert, like that in KC-6 aggregate	5	Not examined
KC-8	Pale yellowish-orange (10YR 8/6) to grayish-orange (10YR 7/4) fine-grained fossiliferous limestone, not forming rims	65	Calcite and very minor quartz
	Very light gray (N8) to yellowish-gray chert (5Y 8/1), chalcedonic	25	Chert predominant, minor or very minor calcite, occasional traces of dolomite
	Light olive-gray (5Y 6/1) limestone	5	Major calcite, moderate chert, very minor clay-mica, traces of feldspar, kaolin or chlorite
	Medium dark gray (N4) fine-grained limestone	3	Major calcite, minor chert, clay-mica; traces of chlorite, feldspar, pyrite
KC-9	Very pale orange (10YR 8/2) soft fine-grained fossiliferous limestone, some pieces having reddish-brown rims in the mortar adjacent to them	70	Calcite, traces of quartz, possible trace of gypsum
	Grayish-orange (10YR 7/4) porous, fossiliferous limestone; fossils darker than matrix and sometimes leached. No rims observed.	15	Calcite, very minor chert, traces of mica
	Light gray (N7) to medium gray (N5) chalcedonic chert	15	Chert with traces of calcite, dolomite
KC-11	Yellowish-gray (5Y 8/1) very fine-grained earthy limestone	50	Calcite, very minor quartz, traces of feldspar, clay-mica
	Light olive-gray (5Y 6/1) limestone, otherwise like the the previous variety	30	Like the above
	Yellowish-gray (5Y 8/1) to dark yellowish-orange (10YR 6/6) vuggy limestone; vugs probably represent leached fossils. A few contained limonite.	10	Calcite, very minor quartz, traces of clay and mica
	Moderate yellowish-brown (10YR 5/4) weathered thin-bedded limestone, in elongated pieces with beds a few millimeters thick. The distribution and amount of insoluble residue varied from piece to piece.	10	Major calcite; very minor quartz, very minor clay-mica with some possible mixed layering with a 14-A clay, traces of feldspar, possible trace of dolomite

widest at the coarse aggregate-mortar interface, dwindling into the surrounding mortar (Fig. 6). X-ray examination of the dark shells and discolored mortar did not show any brucite ($Mg(OH)_2$) and little dolomite was present in the interiors of the rimmed coarse aggregate. A slice of the concrete etched with hydrochloric acid by the procedure of Lemish et al. (8) revealed thin rims, just inside the surfaces of some coarse aggregate particles, less soluble than the surfaces or the interiors (Fig. 7). Two counts of one sawed surface were made at low magnification to determine whether there was any association between the rim phenomena and any evidence of distress. Results of the first count of a 6- by 6½-in. sawed surface parallel to the axis of the core are given in Table 9 and results of the second count are given in Table 10. Chi square, calculated as 49.586 with 2 degrees of freedom, corresponds to a probability less than 0.01 of this degree of association between size and rims arising by chance, showing that rims were more abundant on larger pieces of coarse aggregate. Qualitatively, rims were also more abundant on two darker lithologic varieties which together amounted to one-quarter of the whole coarse aggregate. Rims were least abundant on the commonest lithologic variety in the aggregate (Table 8).

Thin sections of the concrete contained a few highly carbonated areas of mortar, usually partially rimming a coarse aggregate particle and projecting as a short lobe into the mortar. The limestone coarse aggregate ranged from fairly pure and very fine grained to highly fossiliferous and shaly limestone particles, some of which contained coarser-grained recrystallized calcite, and cherty areas. The fine aggregate was coarse natural sand composed of quartz, feldspar, and rock fragments, with occasional chert and cryptocrystalline and glassy rock particles. Most of the sand grains were in the No. 16 to 50 sieve size range. Corroded or partially unhydrated cement grains were abundant. Calcium hydroxide was present both in the paste and at fine aggregate-paste contacts. Chert, and cryptocrystalline and glassy rocks—the poten-

Figure 6. KC-1, sawed surface, three-quarter size. Note dark rims around most of limestone coarse aggregate particles and darker staining of mortar around large limestone particle in lower right corner.

Figure 7. KC-1, sawed surface, three-quarter size, etched with 3N hydrochloric acid. Limestone coarse aggregate particles were etched more than mortar surface itself, and are therefore in negative relief. Note Lemish rim located just inside large limestone particle in lower left center.

tially reactive constituents of the aggregate—showed no signs of having reacted with the alkalies in the cement.

One surface of the prism stored over water (Table 6, Fig. 1) was part of the original surface of the pavement; several white gel spots formed on it. A small gel-filled crack was noted next to a limestone coarse aggregate particle on another surface. No gel appeared on the prism subjected to the Conrow cycle (Table 7, Fig. 3). The gel spots formed on the first prism substantiated the presence in the concrete of ingredients capable of alkali-silica reaction in environments favoring the reaction.

Cores KC-4 and -5, Administration Building, Harlan County Dam, Neb.—Two horizontal cores were drilled from the outside of the north and south walls of the Administration Building at Harlan County Dam, Harlan County, from concrete placed in 1949. The concrete materials were (a) type IA cement; (b) crushed limestone coarse aggregate, Pixley Mine, Independence, Mo.; and (c) Kansas River sand, Stewart Sand and Materials Company plant, Turner, Kan. Chemical analyses of cements from this source, made by the National Bureau of Standards during 1949, indicated total alkali contents, expressed as Na_2O, as high as 0.68 percent. The alkali content of the cement used in the structure is not known.

A sample of limestone (KAN-4 G-6(E-H)) from Pixley Mine, examined at the WES in 1948 (18), was soft limestone of nonuniform texture, with bulk specific gravity in the $^3/_4$-in. to No. 4 size of 2.63; absorption, 1.1 percent, and durability factor with manufactured limestone sand from the same source, 58; with natural fine aggregate from Georgetown, Miss., 30. KC-4 was drilled across a vertical crack below a window outside of the patterned area adjoining the window on the west (Fig. 8). The core arrived as an intact half, from which a deformed reinforcing bar protruded, and several smaller pieces from the other side of the crack. The crack surface was partly

TABLE 9

Aggregate Type	No. of Particles
Limestone coarse aggregate:	
Without rim[1]	38
With rim in rock	20
With lobe or partial rim in mortar	7
With rim in rock, and lobe or partial rim in mortar	32
With crack in rock	2
Chert with adjoining gel pocket	1
Miscellaneous coarse sand grains with evidence of alkali-silica reaction	1
Total	101

[1] Most of the unrimmed particles were very pale orange, fine-grained, high-calcite limestone with minor chert and traces of kaolin-group clay and feldspar.

TABLE 10

Maximum Dimension of Particle (in.)	Rim	No Rim	Total
Up to ¼	8	44	52
¼ to ½	28	14	42
½ to 3	20	0	20
Total	56	58	114

coated with secondary calcium carbonate. KC-5 was an intact core of reinforced concrete. Both cores appeared to have entrained air contents lower than normal with scattered irregular voids up to ¼ in. in diameter. Dark rims on limestone coarse aggregate were common in both cores. The coarse aggregate was 1-in. maximum size limestone, light olive-gray to medium light gray and fine grained, with about 3 percent shaly and fossiliferous pieces; the particles larger than ½-in. maximum diameter had long axes of the exposed sections usually twice as long as the short axes, but the smaller particles were more blocky. In both cores dark rims were conspicuous just inside the peripheries of many of the coarse aggregate particles, more or less concentric with their outer edges. Several relations between the solubilities of different zones appear in Figures 9, 10 and 11. Some coarse aggregate particles show no rims after etching; in others, the center is slightly less soluble than the rim. Many particles in KC-4 (Fig. 9) showed the periphery most deeply etched, the next zone concentric to it narrow, irregular, and the least soluble region of the particle; and the central region more soluble than the intermediate zone but less sol-

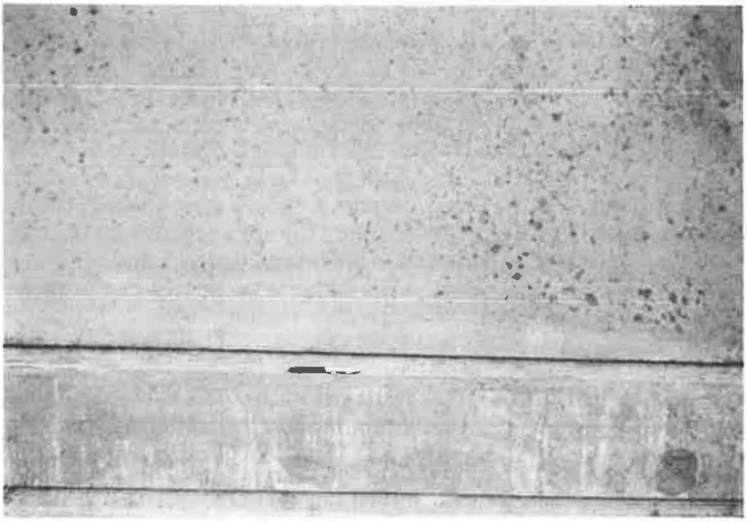


Figure 8. North wall of administration building, Harlan County Dam, Harlan County, Neb., showing mottling of concrete. The ball-point pen is $5^1/_8$ in. long. KC-4 was drilled to left of field shown.

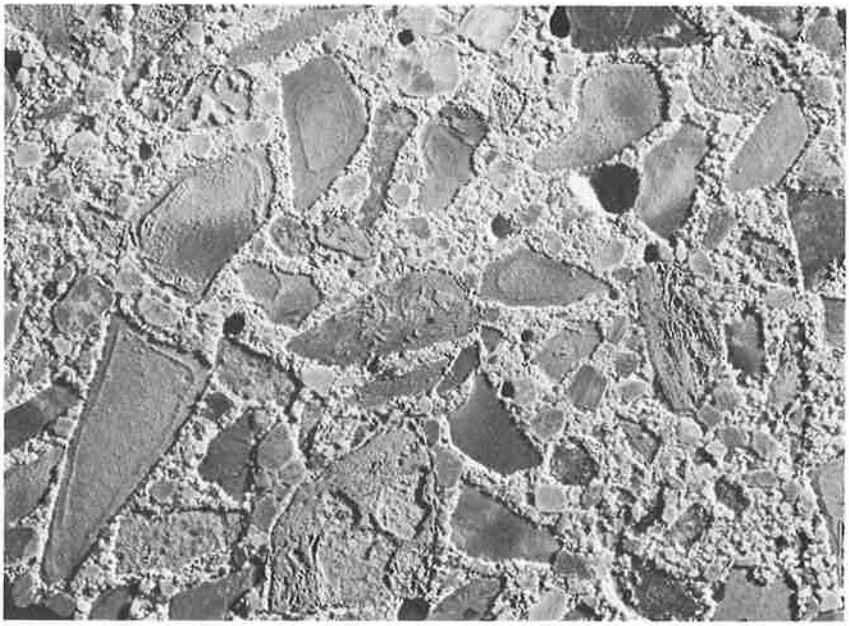


Figure 9. KC-4, sawed surface, x $1\frac{1}{2}$, etched in 3N hydrochloric acid. Limestone particles were etched deeper than rest of surface and are therefore at lower elevations than rest of surface. An excellent example of the Lemish rims that developed on many of these particles is shown in the large, wedge-shaped particle in lower left. Others are present.

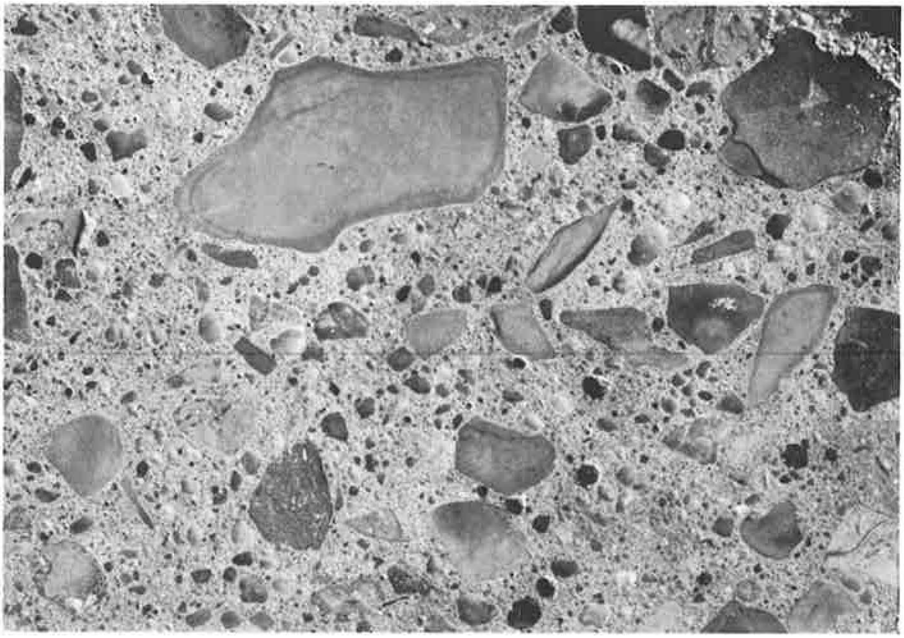


Figure 10. KC-5, sawed surface, x $1\frac{1}{2}$. Concrete in KC-4 and -5 was made from same aggregate and cement combinations; therefore, limestone particles in both exhibit the same type of rims. Compare with Figures 9 and 11.

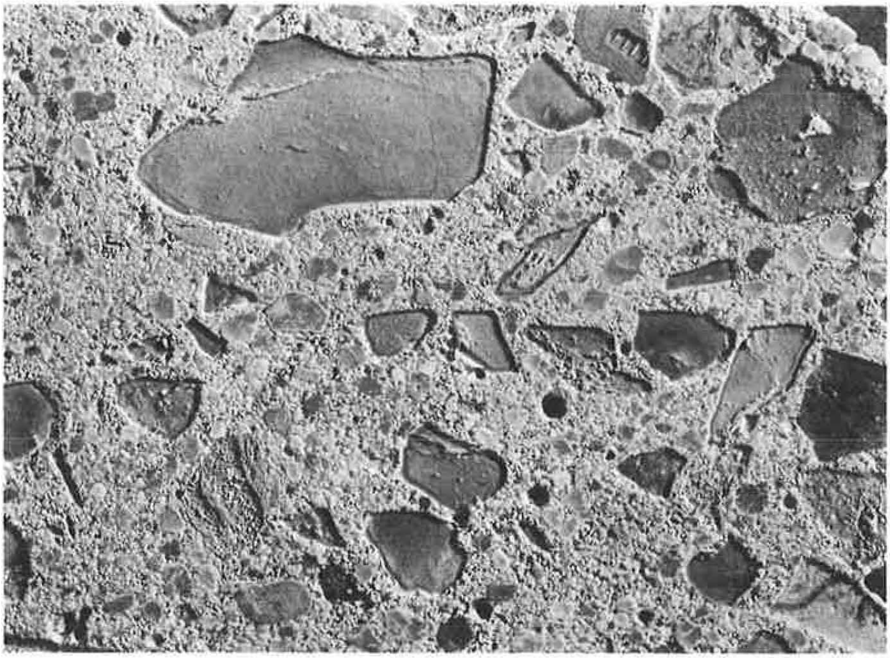


Figure 11. KC-5, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid (same surface as Fig. 10). Note that particles in this photograph displaying Lemish rims are, in most cases, same particles that had dark surface rims in Figure 10.

uble than the outer rim. Coarse aggregate particles were counted on sawed slices from both cores to determine the amount and type of rimming present (Table 11). There was no apparent relation between rimming and particle size. Quartz silt appeared in the limestone as an impurity, recognized in thin sections and by X-ray diffraction, but neither chert nor cherty limestone was found. No dolomite was detectable in the X-ray patterns of the limestone (Table 8). The limestone represented in the 1948 sample contained 2.45 percent insoluble residue, principally quartz, with minor pyrite, and very minor plagioclase, clay-mica, chlorite, and possible kaolin.

X-ray examination of cement paste adjoining a limestone coarse aggregate particle contained substantially more monocarboaluminate than a paste sample farther away from coarse aggregate.

Thin sections of concrete from both cores showed abundant calcium hydroxide in the paste and around many aggregate grains, and substantial carbonation of the mortar at the cement paste-aggregate borders of several of the limestone coarse aggregate particles. The carbonation was heaviest at the paste-aggregate contacts, and usually thinned and faded out a short distance away from the contacts. Calcium hydroxide was generally absent in areas of carbonated paste and at paste-fine aggregate contacts in carbonated areas, but was present on the sides of the particles that were outside the carbonated areas. The resulting texture of the paste was unusual.

TABLE 11

Constituent	Percentage	
	KC-4	KC-5
Limestone:		
No rims or cracks	78	69
With internal rims	17	25
With external rims	2	3
With internal cracks	–	1
With border cracks	–	1
Other (large natural aggregate)	3	1
Total	100	100

Stereomicroscope examination of mounted thin section blanks of these two cores showed an unusual number of microfractures in the cement paste, particularly in the blanks from KC-4, by comparison with blanks of KC-6. The fine aggregate contained a few particles regarded as potentially alkali-silica reactive, but no signs of alkali-silica reaction were observed. Rims of the type present in some of the limestone particles on the sawed surfaces were not recognized in the thin sections. No differences in the limestone particles from the interiors to the borders could be seen, whereas in particles on the sawed surfaces there was a color difference and a difference in solubility in dilute hydrochloric acid just inside the borders of rimmed particles. Most of the limestone particles were fine grained and slightly fossiliferous, with occasional coarser-grained particles, and coarser-grained areas in the finer-grained particles.

No signs of alkali-silica reaction gel were found on the prisms stored at high humidity or those subjected to a Conrow cycle (Tables 6, 7; Figs. 1, 4). The comparison between the behavior of the prism from KC-4 and that from KC-5 in storage at high humidity (Fig. 1) indicated that KC-4 represented concrete that had probably exhibited some of its reactive potential in the structure. The pattern on the outer surface on the north wall of the building (Fig. 8) may represent the result of such expansion. The south wall of the building was not patterned like the north wall; KC-5, from the south wall, retained its expansive potential and exhibited it in the higher expansion it developed and retained in storage over water.

Core KC-6, Garage, Harlan County Dam, Neb.—A horizontal core was drilled from the west wall of the garage building at Harlan County Dam, from concrete placed in 1947 that contained (a) crushed limestone coarse aggregate from the Loring quarries, Bonner Springs, Kan., (b) Republican River sand from the More Sand Company, Junction City, Kan., and (c) type II cement of unknown alkali content. Two samples of type II cement from this mill, analyzed by the National Bureau of Standards during 1947 for projects where low alkali cement was required, had total alkali contents, expressed as Na_2O, between 0.50 and 0.60 percent.

The concrete was well consolidated with slightly higher entrained air content than core KC-4 or -5. Larger entrapped air voids were also numerous; no cracks were observed. The core contained one deformed reinforcing steel bar. No alkali-silica reaction gel was found on the core as received, or after it had been soaked in water for several days.

The crushed stone coarse aggregate consisted of several varieties of limestone, cherty limestone, and chert, graded to 1-in. maximum size. Coarse aggregate particles exposed on sawed surfaces were more blocky with fewer tabular and elongated particles than in cores KC-4 and -5. Light olive-gray and yellowish-brown fine-grained limestone particles made up about 65 percent of the coarse aggregate. A very few of the limestone particles showed rims when sawed surfaces were etched in 3N hydrochloric acid (Figs. 12 and 13).

Light gray, very fine-grained porous particles ranging in composition from calcareous dolomitic sandstone to sandy limestones made up about 20 percent of the coarse aggregate (Table 8). Narrow dark reaction rims located at the aggregate-mortar contacts surrounded most of these particles. The rims were destroyed when the slabs were etched, although the particles were only slightly etched. The etched particles looked porous and spongy (Fig. 13) because the calcite was dissolved out leaving an open network of disseminated chert. Light and medium gray hard dense chert particles with indices of refraction below 1.544 made up about 10 percent of the coarse aggregate. Rims at the mortar-aggregate contact on about one-half of the chert particles were destroyed during etching, although the chert was practically unaffected. The remainder of the coarse aggregate was weathered and shaly limestone.

A count was made on a slice of this core, in which the coarse aggregate particles were classified according to lithology and presence or absence of rims (Table 12). The results given in Table 12 demonstrate that the limestone did not form recognizable rims, but the cherty limestone and chert particles did. The ratio of rimmed to unrimmed particles of cherty limestone was larger than 8 to 1, and the ratio of rimmed to unrimmed particles of chert was 2 to 1. Although no alkali-silica gel was found in this core, the dark rims in the mortar adjoining the cherty limestone and cherty particles

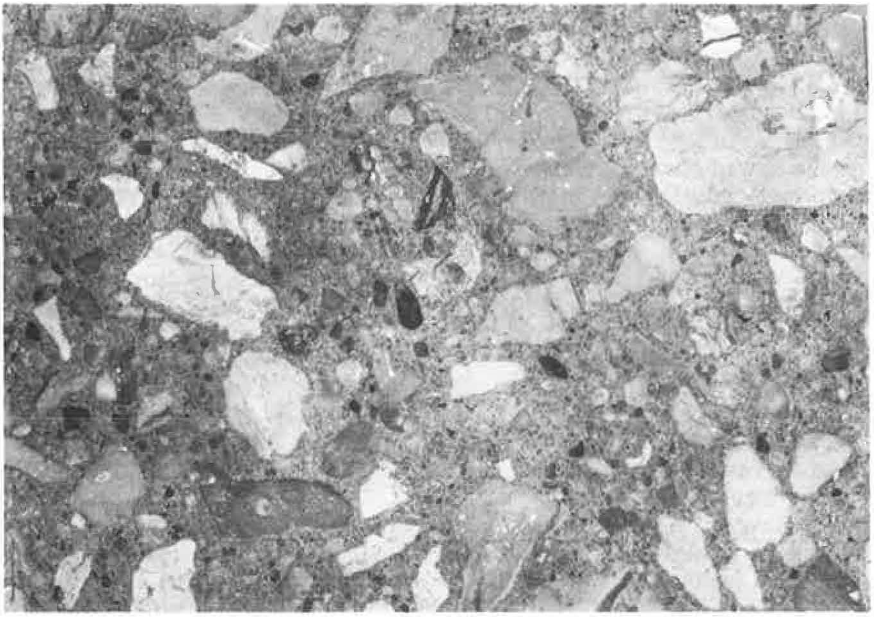


Figure 12. KC-6, sawed surface, x $1\frac{1}{2}$. Narrow rims are present in paste at paste-aggregate contacts of most of lighter coarse aggregate particles, although rims are not readily apparent from this photograph.

Figure 13. KC-6, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid. Light colored, spongy-textured, cherty particles were more resistant to acid attack and are therefore in relief above etched concrete surface. Limestone particles, being less resistant, are in negative relief.

TABLE 12

Constituent	Without Rim		With Rim		Total Observed
	Calculated Theoretical[1]	Observed	Calculated Theoretical[1]	Observed	
Limestone	117.71	143	33.29	2	145
Cherty limestone	30.05	4	8.95	35	39
Chert	9.24	4	2.76	8	12
Total		151		45	196

[1] Assuming observed rims distributed uniformly among coarse aggregate particles without regard to type.

Note: $N = 196$.
Degrees of freedom = 2.
Chi square = 149.480.
Probability of chance occurrence = < 0.01.

are considered a result of reaction between alkalies in the cement and the fine-grained chalcedonic chert in the porous particles. The chalcedonic chert is believed to have acted as a pozzolan in the concrete, using up the available alkalies and thus preventing later expansions caused by alkali-silica or alkali-carbonate reaction.

Thin sections from selected areas of the concrete showed little carbonation of the paste, and no reaction by potentially reactive chert and volcanic rock particles in the sand. Calcium hydroxide crystals were abundant in the paste and partially surrounding fine and most coarse aggregate particles. There was less $Ca(OH)_2$ at the mortar-aggregate contacts of the very fine-grained coarse aggregate particles. Disseminated chert in these particles was generally masked by high birefringence of the calcite. The areas selected for thin sectioning contained several coarse aggregate particles with definite reaction rims, but the rims could be distinguished in thin section only by a general absence of calcium hydroxide in the areas where the rims should have been.

No gel was found on the surfaces of prisms stored at high humidity (Figs. 1 and 4).

Core KC-7, Swimming Pool, Fort Riley, Kan.—A horizontal core was drilled from the wall of the officers' club swimming pool, from concrete placed in 1945 that contained 1-in. maximum size limestone coarse aggregate of unknown source, and Republican River sand from the More Sand Company, Junction City. The type and source of the cement are unknown.

The concrete was not air entrained; it contained two reinforcing steel bars at right angles to each other. The concrete appeared to have a fairly high water-cement ratio, was oversanded, and contained occasional large entrapped air voids. Many of the coarse aggregate particles, and a few of the large sand grains that resembled opaline siltstones, were bordered by narrow rims that ranged from pale to fairly dark. One void partly filled with alkali-silica gel was observed on a sawed surface. No new gel formed on the core surfaces during the several days that it was soaked in water.

The coarse aggregate in KC-7 resembled that in KC-6 and contained the same lithologic varieties in different proportions. Possibly both aggregates came from one formation. KC-7 contained fewer limestone particles readily etched with hydrochloric acid and fewer chert particles, but more calcareous and dolomitic particles with high chert contents and slightly different colors (Table 8; Figs. 12, 13, 14, and 15).

The results of a count of coarse aggregate particles exposed on an unetched slice of this core, in which the particles were classified by lithology and by the presence or absence of rims are given in Table 13. The calculated value of Chi square, 0.237, showed no association between either variety of aggregate and rimming, the reverse of what a similar calculation showed for the aggregate in KC-6. Most of the unrimmed particles were less than ¼ in. in apparent diameter. When sawed surfaces of this core were etched with hydrochloric acid, the rims around the cherty limestone particles were destroyed, as in KC-6.

The etched surfaces of the rimmed limestone particles contained thin rims, at or just inside the aggregate-mortar interfaces (Fig. 15) that were less soluble than the interiors of the particles. Why the limestone particles in KC-7 had rims and those in KC-6 did not is not known. The possibilities include:

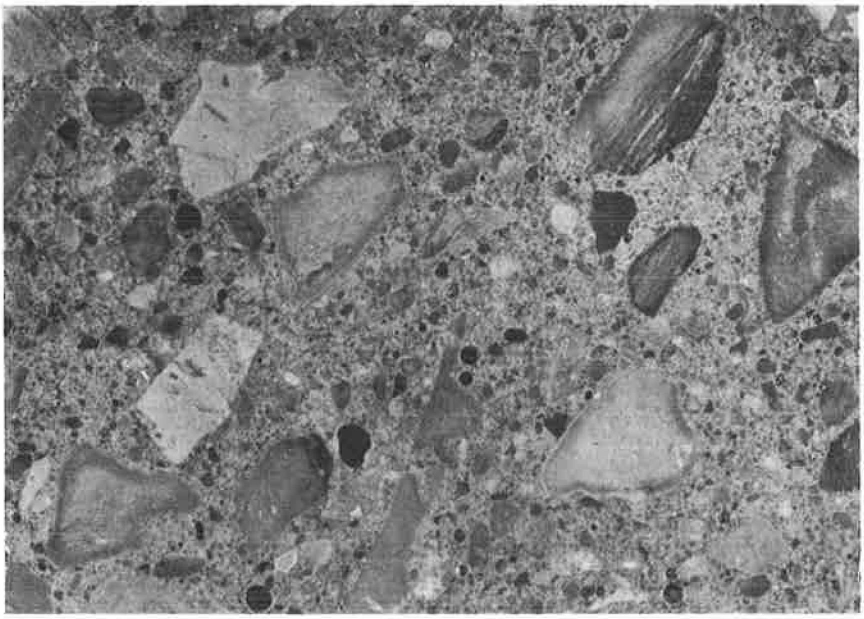


Figure 14. KC-7, sawed surface, x $1\frac{1}{2}$. Lighter colored coarse aggregate particles with rims in mortar immediately surrounding particles are composed of chert and cherty limestone. Darker particles with internal rims are composed of fairly pure limestone.

Figure 15. KC-7, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid. Rims that were present in mortar surrounding cherty particles were destroyed by the acid etch. Rims are present in two limestone particles in upper part of photograph.

TABLE 13

Constituent	Without Rim		With Rim		Total Observed
	Calculated Theoretical	Observed	Calculated Theoretical	Observed	
Limestone	26.38	26	28.62	29	55
Cherty limestone	20.62	21	22.38	22	43
Total		47		51	98

Note: N = 98; degrees of freedom = 1.

1. The alkali content of the cement in KC-6 was relatively lower, in terms of providing alkali to react with cherty limestone, chert, and limestone in the aggregate.
2. The assumption that the two aggregates came from the same formation is wrong, and the comparison between them—which tacitly assumes that they had similar permeability and porosity and similarly reactive chert—is unfounded.
3. Apparently the concrete proportions did differ, and KC-6 contained more and better graded coarse aggregate per unit volume than KC-7; KC-7 apparently had a higher water-cement ratio.
4. The aggregate in KC-6 contained a larger proportion of chert particles than that in KC-7; Table 8 shows 10 percent in KC-6 and 5 percent in KC-7. Both estimates were based on inadequate samples of the same size and should not be accepted as true for the structures, although they are of the right order of magnitude for the cores. Unless the insoluble residue in every piece of calcareous dolomitic sandstone to sandy limestone, all containing chert, that amounted to 20 percent of the coarse aggregate in KC-6, and the insoluble residue in every piece of the calcareous dolomitic chert to cherty calcitic dolomite that amounted to 30 percent of the coarse aggregate in KC-7, were examined, it would not be possible to decide which aggregate contained more total chert. No conclusive evidence of a real difference in total chert content was obtained, although it appeared that KC-6 contained more.
5. The environments of the two concretes were different. KC-6 came from the outer wall of a building above ground. KC-7 came from the wall of a swimming pool, probably below ground, and may have had a better opportunity of becoming saturated, from water in the soil or by failure of the swimming pool liner.

The two concretes may have behaved differently for reasons other than those listed; items 4 through 5 are partly supported by observation or history. It seems unlikely that the two years of age difference between the two concretes was very significant.

Thin sections of areas containing heavily rimmed coarse aggregate particles showed that alkali-silica reaction had occurred between coarse aggregate and paste. Around several cherty limestone particles it was difficult to distinguish between aggregate and mortar, because the mortar bordering the aggregate was heavily carbonated, and dark, dense looking rims of varying widths occupied the vague boundary areas. The interiors of the cherty limestone particles contained porous, cracked, torn areas of types previously associated with and apparently characteristic of reactive aggregate in concrete in which alkali-silica reaction has taken place. Such areas are believed to result from the rock weakening by alkaline solutions and removal of dissolved silica by diffusion or migration. The dark denser rims are a result of deposition of alkali-silica gel in the mortar immediately surrounding the reacted particles. The mortar in the dense rims was heavily carbonated, but the paste as a whole was not. Some alkali-carbonate reaction may have occurred. Calcium hydroxide crystals were abundant in the paste, and around fine aggregate particles located away from the carbonated areas, but were depleted around the reacted cherty limestone particles and perhaps masked in the carbonated paste. Calcium hydroxide crystals were present adjacent to several of the unreacted limestone particles. The potentially reactive constituents present in the fine aggregate were largely unreacted.

Core KC-8, Enlisted Men's Swimming Pool, Fort Riley, Kan.—A vertical core was taken from a World War I sewage plant later converted into an enlisted men's swimming

TABLE 14

Condition	Limestone		Calcareous Chert		Total Observed
	Expected	Observed	Expected	Observed	
No definite rims, no cracks	132.34	152	19.66	0	152
Internal rim with or without internal crack	25.25	3	3.75	26[1]	29
Vague peripheral rim or crack in mortar	17.41	20[2]	2.59	0	20
Total		175		26	201

[1] 15 of 26 particles had interior cracks.
[2] 8 of 20 particles had cracks in mortar.

Note: N = 201; degrees of freedom = 2; Chi square = 177.18. Probability of chance occurrence = < 0.01.

pool at Camp Funsten, Fort Riley. The concrete, placed in 1918, was well consolidated, and only slightly oversanded; no reinforcing steel was exposed in this core. The coarse aggregate was limestone of 1-in. maximum size of unknown source; the fine aggregate came presumably from the Kansas or Republican River near Junction City, and the cement from an unknown source.

Examination of the core, as received, revealed dark rims around cherty coarse aggregate particles and around a few opal-bonded siltstone particles in the fine aggregate. Several of the chert particles were traversed by fine cracks which ran out into the mortar a short distance. No alkali-silica reaction gel was found. After the core had been sliced, soaked in water for several weeks, and the slices dried under gentle heat, several white gel spots were present on the sawed surfaces and in the fine cracks in some cherty particles.

The composition of carbonate coarse aggregate exposed on sawed surfaces of this core is shown in Table 8. The results of a count made on a sawed surface of this core, in which the particles were classified by lithology and the presence or absence of rims and cracks, are given in Table 14. The calculations indicate that: (a) the calcareous chert was associated with interior rims and cracks but the limestone was not, and (b) the limestone was associated with vague peripheral rims and cracks in the adjoining mortar but the calcareous chert was not. The rims and cracks in the cherty particles appeared typical of alkali-silica reaction, and as in KC-6, the evidence summarized here indicated alkali-silica reaction with the cherty coarse aggregate in the concrete.

Sawed and etched surfaces of slices of the core are shown in Figures 16 and 17. Figure 16, the unetched surface, shows the dark internal rims associated with the cherty particles, and shows less clearly vague rims in the mortar surrounding some of the limestone particles. Hydrochloric acid etching destroyed the rims in the chert completely. The mortar bordering the cherty particles was not etched as deeply as mortar in other areas, probably indicating that the mortar around the alkali-silica reactive particles was enriched with alkali-silica gel. The rims that developed on etched surfaces of some limestone particles in KC-1, -4, -5, and -7 were not present on limestone particles in this core; the etched surfaces of the particles were generally smooth and evenly etched.

Most of the area of thin sections from this core was heavily carbonated, but the carbonation was not areally associated with any other recognized feature. Calcium hydroxide was fairly abundant, especially at interfaces between sand grains and paste. No rims were seen in thin section on any of the limestone particles, and only very faint rimming was seen on a few of the cherty particles. Evidence of alkali-silica reaction appeared as cracks in some of the cherty particles and depletion of calcium hydroxide in the adjacent mortar. Small fossils and spherulitic nodules gave the chert a texture which made reacted chert difficult to distinguish from unreacted. The potentially reactive fine aggregate particles had not reacted. Evidence of alkali-silica reaction was much more apparent on sawed slices of this core under low magnification than in thin

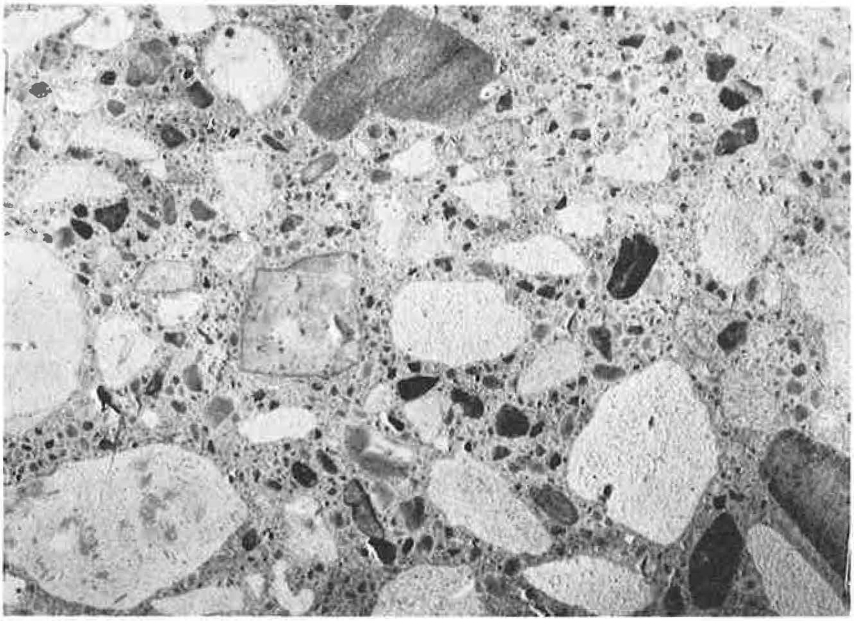


Figure 16. KC-8, sawed surface, x $1\frac{1}{2}$. Particles with dark, narrow reactions rims are composed of chalcedonic chert. Rest of particles, some of which are surrounded by vague rims, are of limestone composition.

Figure 17. KC-8, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid. This is same surface as shown in Figure 18. Limestone particles were heavily etched by acid, whereas the chert particle, located just to left of center, was unaffected.

sections made from the same or adjacent areas of the concrete. No gel or secondary calcite was found on the prism stored at high humidity (Fig. 2); some white gel was found on the surfaces and in mortar adjoining some of the lighter gray calcareous chert particles in the prism subjected to the Conrow cycle (Fig. 5).

Core KC-9, Bridge over Clark's Creek, Geary County, Kan.—A horizontal core was taken from the right abutment of the Geary County highway bridge over Clark's Creek, from reinforced concrete placed in 1926, that contained 2½-in. maximum size crusher-run limestone, probably from the Cottonwood formation, natural sand from the Republican River at Clay Center, and cement of unknown source.

Examination of the core as received, and of slices sawed from it, indicated that little reaction had taken place. No gel or obviously reacted particles were found. The chert particles were not conspicuously rimmed as in core KC-8; some of the larger limestone particles were partially rimmed by darker reddish-brown mortar borders that blended within short distances into the normal gray mortar of the rest of the core. The discolorations in the mortar were somewhat like those around some of the limestone particles in KC-1, but those in KC-9 were not as conspicuous. At low magnification a few hairline cracks were observed on sawed surfaces; the cracks appeared to originate in large coarse aggregate particles, and extended out into the mortar, running around and through other coarse aggregate particles, before fading out. The cracks were not lined with reaction products. They are believed to have been present in the concrete core before sawing. The coarse aggregate ranged from about 2½-in. maximum size down into sand sizes, with most of the larger particles larger than 1½ in. About one-half of a surface sawed normal to the length of the core contained four or five coarse aggregate particles (Figs. 18 and 19). Hydrochloric acid etching destroyed rims in the mortar surrounding the limestone particles, and revealed rims similar to those in KC-1, -4, -5, and -7 on several of the limestone particles (Fig. 19).

The results of a count made on a sawed surface in which the particles were classified by lithology and the presence or absence of rims or cracks are given in Table 15. The calculations indicated that rims and cracks were associated with the cherty particles and not with the limestone. These rims and cracks were attributed to a reaction between alkalies in the cement and soluble silica present in the chert.

The mortar in thin sections from selected areas of this concrete core was only slightly carbonated, with abundant large unhydrated cement grains containing clusters of alite and belite crystals. Apparently the cement used was coarser than modern cements. Calcium hydroxide was abundant in the paste and at the paste-aggregate contacts of siliceous fine aggregate and some limestone coarse aggregate particles.

Several chert particles were either wholly or partially surrounded by dark gel-soaked rims produced by alkali-silica reaction. One such particle was bordered by a short narrow gel-filled crack along the contact between the particle and paste. Most of the reacted chert particles contained short cracks which originated in the particles and stopped at the aggregate-paste contact or extended a short distance into the paste. Calcium hydroxide was absent in the gel-soaked rims and along the inner sides of paste-aggregate contacts of fine aggregate particles in or near the rims, but was present along the opposide sides of such particles, away from the rims. The reddish-brown mortar borders around some limestone particles were seen in the thin sections as highly carbonated areas in which no calcium hydroxide was present. The narrow carbonate rims usually had one or more lobes or tongues extending out into the mortar. These rims were probably the result of an alkali-carbonate reaction.

Several longer old cracks in the mortar of some thin sections were bordered by highly carbonated paste. The potentially reactive fine aggregate particles, present in very minor amounts, had not reacted.

Core KC-11, Boiler Plant, Fort Riley, Kan.—A horizontal core was drilled from the north wall of the Fort Riley hospital boiler-plant compressor room. The reinforced concrete placed in 1955 contained 1-in. maximum size limestone from the Towanda formation, quarried near Milford; Republican River sand from the More Sand Company, Junction City; and type I or IA portland cement. Mill certificates during the construction period indicated that the cement had (a) alkali contents, expressed as Na_2O, ranging between 0.46 and 0.51 percent; (b) MgO, between 2.85 and 3.08 percent; and (c) auto-

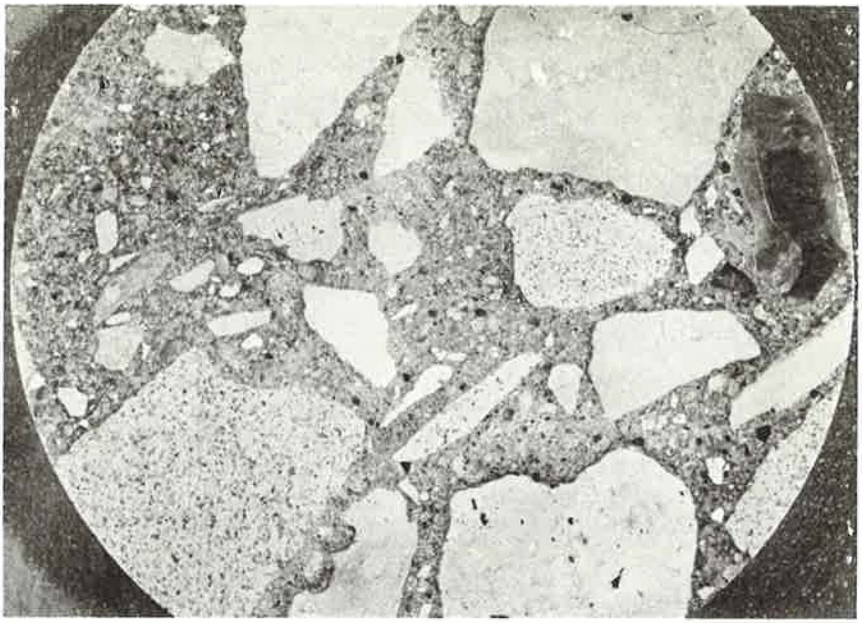


Figure 18. KC-9, sawed surface, three-quarter size. Reddish-brown carbonated rims associated with some of the limestone particles are illustrated by dark mortar rim around large limestone particle in lower right. Others are present but are less distinct. Dark particle in upper extreme right is chalcedonic chert.

Figure 19. KC-9, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid. Large limestone particle in center contains a shell of less soluble material along two sides of particle, a slight distance inside aggregate-mortar contact. Chert particles were unaffected by acid.

TABLE 15

Constituent	No Rim, No Cracks		With Internal or External Rim, With or Without Cracks[1]		Total Observed
	Expected	Observed	Expected	Observed	
Limestone	114.26	123	14.74	6	129
Chert	9.74	1	1.26	10	11
Total		124		16	140

[1] External rims in mortar around 5 limestones; cracks in 3 cherts; no cracks in limestone.

Note: N = 140; degrees of freedom = 1; Chi square = 66.22; probability of chance occurrence = < 0.01.

clave expansions of about 0.095 percent. The concrete was well consolidated and in good physical condition. The entrained air content was rather low; few entrapped air voids were observed on sawed surfaces; no rimmed or reacted coarse aggregate particles were noted; and only one reacted opaline siltstone particle was seen on a sawed surface.

The finished surface of the core, representing the outer surface of the wall, was mottled light gray and olive-gray (Fig. 20). The mottling was caused by variations in bond between the wood-formed surface and a cement paste rendering put on to improve the appearance of the wall. Part of the rendering adhered and part did not adhere to

Figure 20. KC-11, finished wall surface, three-quarter size. Mottled appearance of surface is due to poor bond between wood-formed surface and rubbed on cement paste. Light areas are rubbed cement still adhering to original surface. Impression of wood form is apparent. Irregular dark lines are penciled traces of fine shrinkage cracks.

the concrete, producing the mottled appearance. Several thin very shallow shrinkage cracks were observed in the mortar and rubbed cement paste when the surface was viewed at low magnification (×10).

Crushed limestone aggregate from the Shandy quarry, 0.8 miles west of Milford, in the Towanda formation, the source used in the boiler plant of the Fort Riley hospital, was tested in 1956 by the Missouri River Division Laboratory, with the following results: specific gravity, 2.51; absorption, 1.9 percent; durability factor with Georgetown, Miss. sand, 57, and with Big Blue River sand, 50. The petrographic examination found 74 percent dense limestone, 24 percent porous limestone, and 2 percent shaly limestone. Additional tests of limestone from this source in 1958, 1959, and 1960 indicated that the quality of the aggregate was similar.

The apparent proportions of the three varieties of limestone (Table 8) in this core agree fairly well with the composition reported by the MRD Laboratory. The small amount of quartz identified by X-ray diffraction and seen in thin sections was present as detrital quartz grains and not as chalcedonic chert. The results of a count on a sawed surface of the core are given in Table 16.

Unetched and etched sawed surfaces of KC-11 are shown in Figures 21 and 22. The etched surfaces of most of the coarse aggregate particles were smooth and even. The vuggy particles were more irregular and pocked because of holes left by previously

TABLE 16

Constituent	Percent
Limestone, no rims, no cracks[1]	91
Limestone, with vague external rims	2
Limestone, with internal cracks[2]	2
Other (large fine aggregate)	5
Total	100

[1] 9% of particles were vuggy.

[2] Cracks were probably produced before aggregate was used in concrete.

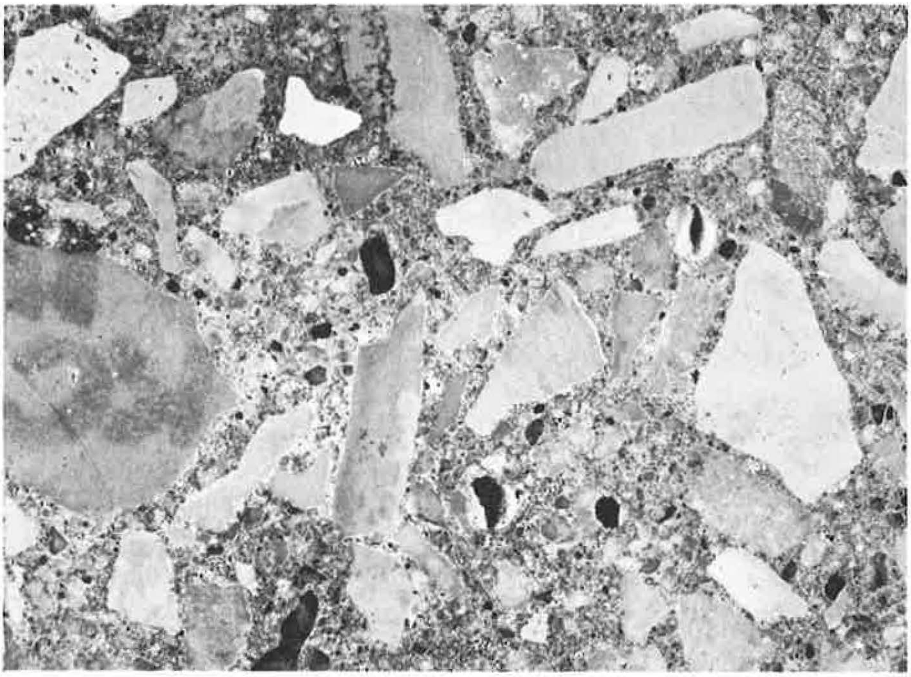


Figure 21. KC-11, sawed surface, × 1½. No coarse aggregate particles are rimmed. One rimmed opaline siltstone particle is located just beneath tabular limestone particle in upper right. Dark areas in large air voids are shadows caused by crosslighting.

Figure 22. KC-11, sawed surface, x $1\frac{1}{2}$, etched with 3N hydrochloric acid. Acid made a smooth, even etch on most particles. Pocked appearance of some particles is due to dissolved-out fossils. All coarse aggregate particles are in negative relief.

leached fossils. None of the etched particles showed rims of any kind. The limestone aggregate in this structure had been almost totally unaffected by any of the types of reactions known to occur between cement paste and carbonate aggregate particles when the core was taken. The prism cut from the core and stored at high humidity for 19 months had developed fairly conspicuous rims between 12 months and 19 months of storage; no rims were found when the prism was sliced. (The expansion at the time when the prism was sawed was 0.067 percent, while the maximum attained has been 0.098 percent.) The rims were interpreted as a leaching phenomenon, because they were confined to the outer surface of the prism.

X-ray diffraction examination of paste concentrates from the prism stored at high humidity showed that additional high-sulfate calcium sulfoaluminate, and calcium monosulfoaluminate had formed; the failure to find increased calcium monocarboaluminate was surprising.

Thin sections of this concrete were characterized by abundant calcium hydroxide in the paste, at the contacts between paste and aggregate particles, and lining many of the entrained air voids. Virtually no secondary carbonation of the mortar had developed. The limestone coarse aggregate particles had not developed carbonate rims. Almost all the potentially reactive fine aggregate particles—chert and glassy volcanic rocks—were unreacted. The thin sections of this concrete at the age of six years indicated that normal hydration had taken place, producing a normal texture, degree of hydration, and appearance of the concrete.

One large gel exudation was found on the surface of the prism subjected to the Conrow test after it had been soaked in water only three days. The exudation continued to grow, and several small gel pockets formed on the surface and in surface air voids during the ten months that the prism was measured. No gel deposits or rims were observed on the surfaces of the prism stored at high humidity during the first ten months of storage;

the rims observed at 19 months have already been described. The prism from KC-11 developed the second highest expansion in storage over water and higher expansion in the Conrow cycle than any of the other concretes tested.

CONCLUSIONS

Cores from seven structures in Kansas and Nebraska, representing concrete that ranged in age from 6 to 43 years at the time of examination, all contained carbonate coarse aggregate and natural fine aggregate, and all showed evidence of a chemical reaction or of more than one chemical reaction, exclusive of those found in normal hydration of cement.

All of the fine aggregates contained the reactive constitutents typical of natural aggregates in northeastern Kansas—opal in the form of calcareous opal or opal-bonded siltstone, chert, and glassy volcanic rocks. In large measure, these minor reactive constituents of the sands had not reacted or had reacted only to a minor degree. In all seven cases, the constituents showing most reaction were constitutents of the coarse aggregates.

Two sawed prisms were prepared from each of six cores representing five of the structures; ball bearings were cemented to each end of each prism as reference points. One prism from each core was stored over water at high relative humidity; the other was subjected to a cycle like that in the Conrow test (ASTM Designation: C 342), but with slightly greater fluctuations in the temperature of the storage room than allowed by the method.

The length-change tests were made because field examination of some of these structures had not shown any unequivocal evidence of expansion, although it was known that all of the sands contained alkali-silica reactive constituents. Inasmuch as the structures are located in areas where the average precipitation ranged from 21 to 32 in. per year, it seemed desirable to investigate the question, whether the concretes had significant expansive potential if moisture were supplied. Prisms sawed from the cores offered the only available test specimens, because the aggregate and cement sources for several of the concretes were not known.

Although the meaning of the length changes developed by the concrete prisms is not entirely clear, because the alkali contents of the cements are not known, the following points are clear (Tables 6 and 7):

1. All of the concretes expanded more than 0.05 percent by 88 days of storage at high relative humidity.
2. Three of them thereafter either shrank or at least slowed the rate of length gain substantially, but three continued to grow, and reached length changes of 0.098 or 0.099 at 340 days or one year.
3. One of the three was KC-8, 43-year-old concrete, which, because of the amount of perceptible alkali-silica reaction that it exhibited in the as-received condition, was believed to have reacted as much as it was likely to before the prism was placed in high humidity. The other prism sawed from the same core reached an expansion of 0.168 percent in the Conrow cycle.
4. The other two concretes that expanded the most were KC-5, from the only structure in the group that is known to have shown any outward peculiarity of its concrete (Fig. 8). KC-4, from the same structure, but from the mottled wall of that structure, showed considerably less expansion, suggesting that this concrete had used more of its expansive and reactive potential at the time when the core was taken.
5. KC-11, from the youngest structure in the group, expanded to the maximum degree found both in storage at high relative humidity and in the Conrow cycle. This concrete contained the aggregate combination that had been approved for use in the concrete in Milford Dam.

The major difficulty in the examination of these seven concrete cores, which all showed evidence of chemical reaction, lay in distinguishing which reactions were present in each concrete, and which should be regarded as significant in the performance of the concrete. Four of the structures—those represented by KC-1, -4, -5, and -6,

TABLE 17

CONCRETES FROM STRUCTURES IN KANSAS AND NEBRASKA

Characteristic	Specimen KC-8	Specimen KC-1	Specimen KC-9	Specimen KC-7	Specimen KC-6	Specimen KC-4, -5	Specimen KC-11
Age (yr)	43	37	34	16	14	12	6
Rainfall at site (in./yr)	32	26	32	32	21	21	32
Type of structure	Swimming pool wall	Pavement	Bridge abutment	Swimming-pool wall	Bldg. wall above grade	Bldg. wall above grade	Bldg. wall above grade
Chert in coarse aggregate	25+% chalcedonic	Minor in all varieties	15+% chalcedonic	Moderate to major chert in 30% of total, the variety ranging from calcareous dolomitic chert to cherty calcareous dolomite; minor chert in limestone making 50% of total; 5% chert.	10% chalcedonic chert; moderate chert in 20% of total ranging from calcareous dolomitic sandstone to sandy limestone; very minor to traces in the 65% of fine-grained limestone.	Not detected	Not detected
Dolomite in coarse aggregate	Traces in the 25% of chert	Minor in two varieties that total 25%	Trace in the 15% of chert	Very minor in the 50% of fine-grained limestone; moderate to major in the 30% of the total containing most of the chert.	Major to very minor in the 20% ranging from sandstone to sandy limestone; minor to traces in the rest.	Not detected	Not detected
Estimated or determined insoluble residue	Low in 68% of aggregate.	Medium	Low in 85% of aggregate.	Low in 65% of the aggregate.	Low in 70% of the aggregate.	2.45%, qtz,[1] pyrite, feldspar, clays.	Low
Expansion of prisms stored at high humidity at 1 yr	0.098 at 340 days	0.063	Not tested	Not tested	0.067	KC-4: 0.066% KC-5: 0.099%	0.098% at 340 days
Expansion of prisms exposed to Conrow cycle at 1 yr	0.168%	0.034%	Not tested	Not tested	0.057% at 333 days[2]	KC-4: 0.079% KC-5: 0.061%	0.241
Monocarboaluminate in mortar concentrate:						KC-4 KC-5	
passing No. 100 sieve	Minor[2]	Trace[3]	Minor[2]	Minor[2]	Minor	Minor Minor-	Minor-
retained on No. 100 sieve	Trace[2]	Not detected	Minor[2]	Trace	Trace	Trace Trace	Trace
Carbonation of mortar	Widespread, patchy; no association with other features detected.	Carbonated rims and lobes projecting into mortar, around two varieties of limestone making 25% of total.	Some widespread carbonation; some rimming limestone as in KC-1.	As in KC-1.	Negligible; association with other features not detected.	Along cracks in KC-4; as in KC-1 in both cores.	Absent
Alkali-silica reaction with coarse aggregate	Rims on calcareous chert; internal cracks in most of the rimmed chert.	Evidence not clear.	Rims on chert and internal cracks most of the rimmed chert.	Rims on the cherty calcareous dolomite ranging to calcareous dolomitic chert.	Rims on the cherty limestone and chert.	Evidence not clear in either core; no alkali-silica reactive constituent.	Not with the coarse aggregate; no alkali-silica-reactive constituent.
Alkali-carbonate reaction with coarse aggregate	Vague rims in mortar surrounding some calcitic limestone.	Rims and lobes in mortar surrounding two dolomitic varieties making 25% of total.	Rims bordering some calcitic limestone.	Etched surfaces (in Fig. 15) shows one particle with periphery less soluble than interior.	Not recognized.	Conspicuous and fairly common in calcitic limestone.	Not recognized in the core; formed on outer surface of prism stored at high humidity.
Coarse aggregate constituents involved in reaction	Calcareous chert; calcitic limestone to a minor extent.	Large pieces of dolomitic clayey-cherty limestone.	Chert; calcitic limestone to a minor extent.	Calcareous dolomitic chert to cherty calcareous dolomite; limestone.	Cherty limestone and chert.	Fine-grained calcitic limestone.	Fine-grained calcitic limestone (in prism stored at high humidity.
Major reaction	Alkali-silica	A carbonate reaction involving the varieties containing minor dolomite.	Alkali-silica	Alkali-silica and alkali-carbonate reactions.	Alkali-silica	Alkali-carbonate with calcitic limestone.	Alkali-carbonate with calcitic limestone.
Minor reaction	Alkali-carbonate with calcitic limestone.	Very minor alkali-silica reaction with fine aggregate.	Alkali-carbonate with calcitic limestone.	The two above appear virtually equal.	None recognized.	None recognized.	None recognized.

[1] Determined on 153.6 g of sample acquired in 1948.
[2] Reference point fell out, invalidating next reading.
[3] High in calcium sulfoaluminate among these concretes.

had been inspected by the senior author; the only one in which the concrete looked odd was the administration building at Harlan County Dam, represented by cores KC-4 and KC-5. All four structures were presented as examples of concrete in good condition. The other three structures were not described as showing evidence of improper behavior by the concrete, but on the other hand none was located on a poorly drained subgrade and all were exposed to less than average annual precipitation. When rims were found on the surfaces of KC-1, -4, and -5, it was necessary to discover how many of the concretes showed evidence of alkali-carbonate reaction, as well as or instead of the alkali-silica reaction with fine aggregate, that had been regarded as probable.

Because of the indications of alkali-carbonate reaction, the composition of the coarse aggregate was investigated in detail and evidence of rim formation and of dedolomitization was sought. Tests of association, between composition of individual pieces of coarse aggregate and various phenomena of rimming and cracking that were found, served in some cases to distinguish those lithologic varieties that were related to reaction from those that were not, and permitted conclusions on which reaction was the more important in concrete in which more than one was detected.

The concretes may be sorted into four groups; evidence other than the calculations of Chi square that assisted in the sorting is summarized in Table 17.

1. Reaction principally involving dolomitic limestone. KC-1 contained two varieties of aggregate in which dolomite was a minor constituent; chert was a minor constituent of all varieties. Rims within coarse aggregate particles, visible on unetched surfaces as well as on etched ones, and staining and carbonation of the mortar around the coarse aggregate, were associated with the two limestone varieties containing dolomite, and not with the major variety that did not contain dolomite. The mortar from this concrete was low in calcium monocarboaluminate as compared to the rest of the concretes, and high, by comparison, in high-sulfate calcium sulfoaluminate. Brucite was not detected in the rims on the coarse aggregate or in the surrounding paste. The existence of alkali-silica reaction in the cherty dolomitic limestone cannot be demonstrated, although evidence of minor alkali-silica reaction with some of the fine aggregate was seen.
2. Carbonate reactions with calcitic limestone. KC-4 and -5, and KC-11, each contained coarse aggregates in which dolomite was a trace constituent at the most, and in which chert was not detected. The insoluble residue in aggregate from the source of that used in KC-4 and KC-5, represented by a sample taken one year earlier than the concrete was placed, was 2.45 percent, mostly quartz silt; the insoluble residue in the coarse aggregate in KC-11 was as low or lower. KC-5 and KC-11 prisms expanded in storage at high humidity to 0.099 and 0.098 percent at one year. KC-4 did not expand beyond 0.066 percent at one year, but came from the side of the building on which the concrete was visibly affected. KC-4 and KC-5 manifested rims on etched surfaces which were more soluble than the interior of the particles; it is unlikely that the removal of so small a quantity of insoluble residue as this coarse aggregate contained would produce so apparent a difference in solubility.
3. Alkali-carbonate and alkali-silica reactions equal. The coarse aggregate of KC-7 contained both chert and dolomite in one variety of rock ranging from calcareous dolomitic chert to cherty calcareous dolomite; it also contained 5 percent of chert particles, and minor chert in the limestone. No association between lithology and rims was recognized, because all varieties of aggregate showed some kind of rim in about one-half of the particles, and cherty regions in the coarse aggregate were cracked and torn in thin sections in the manner characteristic of alkali-silica reacted chert. The type or types of carbonate reactions are not known.
4. Major alkali-silica reaction, alkali-carbonate reaction minor or absent. KC-8 coarse aggregate contained 25 percent chalcedonic chert; dolomite was present in traces in the chert but was not found in the limestone; KC-9 coarse aggregate contained 15 percent of chalcedonic chert with traces of dolomite but no other dolomite; KC-6 coarse aggregate contained 10 percent chalcedonic chert and moderate amounts of chert in 20 percent of the aggregate that ranged from calcareous dolomitic sandstone to sandy limestone. KC-8 showed reaction with the chert, accompanied by some crack-

ing, and minor development of rimming in mortar around calcitic limestone; KC-9 showed rims on the chert and minor development of rims in the mortar; KC-6 showed conspicuously more rimming of limestone containing disseminated chert than of chert, and negligible rimming of limestone. No reaction other than alkali-silica reaction was established in the case of KC-6. The structure from which this core came, appeared to be in good physical condition; apparently the alkali-silica reaction was not harmful, and was in fact concluded to be beneficial, by comparison with the condition of KC-4 from the adjoining building.

DISCUSSION

The first part of this paper describes an instance in which alkali-silica reaction and the alkali-carbonate reaction, dedolomitization, were found to have occurred in the same laboratory specimens, but the alkali-silica reaction was apparently confined to opaline montmorillonitic shale and the dedolomitization reaction was confined to dolomitic limestones, and was manifested in the development of brucite in the mortar surrounding the dolomitic limestone particles.

The second part describes seven more complicated situations involving field concretes that all contained fine aggregates capable of some alkali-silica reaction, and carbonate coarse aggregates with and without dolomite, and with and without chalcedonic chert. None of the concretes was in great distress. The concrete from the structure that showed visible peculiarities of the concrete contained a quite pure calcitic limestone with no more than traces of dolomite and no chert; it was concluded that a reaction affecting the calcitic limestone was the only recognized cause of the distress. Prisms from this concrete and from another structure made from a similar limestone expanded 0.10 percent in one year of storage at high humidity. In one case, the particles of coarse aggregate showing the most evidence of reaction were those of two varieties containing dolomite; the calcitic limestone was not affected. The dolomitic varieties also were clayey and cherty. Alkali-silica and alkali-carbonate reactions were of apparently equal importance in one structure; the types of alkali-carbonate reaction are not known. Alkali-silica reaction predominated over alkali-carbonate reaction with calcitic limestone in two cases; in a third, the major alkali-silica reaction was not accompanied by alkali-carbonate reaction.

The principal difficulties in reaching any conclusions with regard to the concretes discussed in the second part of the paper lie, first, in recognizing that so many different reactions and combinations of reactions were represented in so small a group of concretes that had been expected to be comparable in many respects, and in developing evidence that would permit conclusions about the relative importance of reactions when more than one was involved.

The second part demonstrates that the question of beneficial effects of the addition of carbonate coarse aggregates to the sands and sand-gravels of the Kansas-Nebraska area is a very complex one in which the chemical reactivity of the carbonate coarse aggregates may be of the greatest significance.

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General Discussion

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Hadley points out that three mechanisms have been proposed to account for the expansions of carbonate rocks immersed in solutions of alkali hydroxides or when used as aggregates in concrete made with cements containing alkalies above about 0.4 percent. This discussion pertains to the mechanism by which direct enlargement of the crystals of dolomite is believed to be responsible for much, if not all, of the expansion obtained with dolomitic rocks.

In 1962 (1), the dedolomitization reaction was briefly discussed and it was pointed out that for this reaction to produce expansion it was necessary for the hydroxyl and alkali metal ions to penetrate the lattice of the dolomite crystal and enlarge the crystal. When the crystal is embedded in a rigid matrix of hardened cement paste in a concrete structure, such enlargement of the crystal would exert pressure on this matrix and this pressure would be expected to cause expansion of the concrete structure.

This mechanism explains why the alkali-dolomite reaction can cause expansion of concrete, but it does not explain why samples of rock immersed in solutions of different alkali hydroxides show different amounts of expansion. For an explanation of this, one must examine the mechanism involved when an ionic compound dissolves in water.

When a crystal of a compound, such as one represented by the formula CA in which C is a cation and A is an anion, is immersed in water, water molecules penetrate the crystal lattice and force the cations and anions apart. After sufficient water has entered the lattice to overcome the ionic forces that hold the ions in the lattice, each ion with its share of the water diffuses into the water as the hydrated ion. During this process of imbibing water, the crystal is enlarged. If the crystal is confined in the rigid matrix of hardened cement paste in a concrete structure, this enlargement caused by the solution process will exert pressure against the confining paste and cause the concrete structure to expand.

When a dolomite crystal is immersed in a solution of sodium hydroxide, hydroxyl ions penetrate, for example, the lattice of the magnesium carbonate and become associated with the magnesium ions. Because electrical neutrality must be maintained, an equal number of sodium ions penetrate the lattice and become associated with the carbonate ions. Water molecules then penetrate the lattice and tend to dissolve the crystal. The sodium and carbonate ions behave in a manner similiar to that of the ionic compound CA discussed previously.

At normal atmospheric temperatures, sodium carbonate in a limited amount of water forms a hydrated compound with the composition $Na_2CO_3 \cdot 10H_2O$. In greater amounts of water this compound dissolves completely. From this it is seen that in a crystal of sodium carbonate, one molecule of sodium carbonate can combine with ten molecules of water to form a solid compound before sufficient water can be imbibed by the crystal to start the process of forcing the cations and anions apart to the extent necessary for the crystal to dissolve.

Samples of dolomite immersed in a solution of potassium hydroxide expanded less, in a given period of time, than did samples immersed in sodium hydroxide. At normal atmospheric temperatures, potassium carbonate in a limited amount of water forms a hydrate with the formula $K_2CO_3 \cdot 2H_2O$. Hence instead of having to imbibe ten molecules of water per molecule of carbonate, as required by sodium carbonate before the solution process can start, the solution process for potassium carbonate can start after two molecules of water have penetrated the crystal lattice.

Immersion of the dolomite samples in lithium hydroxide produced less expansion than was obtained with immersion in solutions of potassium hydroxide. At normal atmospheric temperatures, lithium carbonate does not form a hydrated compound. Hence lithium carbonate has to imbibe less water than either potassium or sodium carbonate before solution is effected.

When Sherwood and Newlon immersed samples of the minerals calcite and dolomite in concentrated solutions of the hydroxides, they observed gaylussite ($CaNa_2(CO_3)_2 \cdot 5H_2O$), buetschliite ($Ca_2K_6(CO_3)_5 \cdot 6H_2O$) and portlandite ($Ca(OH)_2$) in the reaction products. These results show that calcite can react with alkali hydroxides. As water in the cement paste is used up by reaction with the cement minerals and as water evaporates from the concrete, the concentration of the alkalies in the solution in the pores of the hardened cement paste and in the pores of the aggregate becomes rather high. Therefore it seems necessary to conclude that the calcite fraction in the fine-grained reactive dolomitic rocks may contribute to the expansions in concrete. This also suggests that the alkali hydroxides may not be regenerated by the reaction illustrated by the following equation: $M_2CO_3 + Ca(OH)_2 = 2MOH + CaCO_3$ in which M is an alkali metal such as sodium and potassium.

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The question raised by Dr. Hansen regarding the regeneration of alkali after the dedolomitization reaction, together with reports concerning the occurrence of new types of reaction rims in rocks with low dolomite content make it desirable to consider the stability of solid calcium carbonate (calcite) in the presence of cement hydration products.

For reasons to be described it is believed that considerable regeneration of alkali can occur. It is also believed that in the attainment of equilibrium considerable reaction can occur between calcite and cement hydration products. It must be remembered, however, that such factors as texture and impermeability of a rock may result in exceedingly slow reactions so that many years may be required for the attainment of equilibrium.

Recent results at the PCA Laboratories and elsewhere have provided more details of the mechanism for alkali regeneration originally proposed by Hadley in general form. It appears that, for a cement containing appreciable tricalcium aluminate, the alkali regeneration would result initially and primarily from the formation of calcium carboaluminate hydrate, a material which was observed by Hadley (1) at the paste-aggregate interface in cylinders of expansive rock coated with cement paste. The reaction would proceed according to an equation of the type:

$$M_2CO_3 + C_4AH_{19} \rightarrow 2MOH + C_3A \cdot CaCO_3 \cdot 12H_2O + 6H_2O$$

in which M stands for K, Na, or Li and the compound C_4AH_{19} is used as one of the typical hydration states of tricalcium aluminate.

Calcium carboaluminate hydrate is a material which is much less soluble than calcite. Experiments reported in the literature (2, 3) have shown that this compound will form even in the presence of sulfate ion. Formation of this material does not consume alkali, in contrast to formation of gaylussite or buetschliite. The calcium carboaluminate hydrate, unlike the high sulfate form of calcium sulfoaluminate (ettringite), does not show high solubility in alkali. In a particular experiment, X-ray diffraction showed that a sample withstood exposure to 10 percent sodium hydroxide solution for 14 days without decrease in intensity of the pattern and without formation of crystalline decomposition or reaction products. This lack of reaction cannot be attributed merely to a low reaction velocity, because the compound forms and crystallizes readily by reaction of C_3A with calcite in the presence of alkalies. Thus the regeneration of alkali must take place at least until most or all of the tricalcium aluminate hydration products have been carbonated. Although the exact equilibrium point for the sulfate and carbonated hydration products in the presence of each other has not been determined, the relatively high solubility of the sulfate in alkali has been previously reported (4).

Consideration must next be given to the hydration products of the ferrite phase. Little is known about these materials. Exploratory studies in the PCA Laboratories have, however, demonstrated that hydration of an intimate mixture of calcite and tetracalcium aluminoferrite will produce calcium carboaluminate hydrate and perhaps even a hydrated carboferrite, but the extent of reaction in the presence of alkalies and sulfate ion, such as would occur in the environment in concrete, has not as yet been investigated. The existence of these reactions indicates that considerably more regeneration of alkali or reaction of calcite may occur than can be expected from merely the C_3A content of a cement.

The relative insolubility of the carbonated aluminate hydrate would also lead one to expect relatively high potential reactivity of calcite in concrete aggregate with cement hydration products, as has been observed in laboratory studies (2). The scarcity of reports of such reactions in the literature would lead one to believe that the limestone aggregates normally used in sound concrete are sufficiently impermeable and unreactive to permit only very limited surface reactions. The occurrence of the carboaluminate in Hadley's work with reactive rock of relatively porous texture would make further study of these equilibria in relation to rim formation very interesting.

As a further point of reference in these considerations, the reaction of alkali with calcium carbonate has been studied in some detail. It is recognized that this reaction would not become significant until and unless the reactions already described have been completed. However, the important parameters in this system have been measured so that detailed calculations for dilute solutions can be made. The equilibrium point in this system can be most easily appreciated when it is recalled that a standard method for the commercial production of sodium hydroxide has for many years been the reaction between sodium carbonate and lime, the so-called "causticization" reaction (5). The equilibrium in this process has been studied intensively, but the results are of marginal use here because they apply to reaction as carried out commercially at elevated temperatures. Few direct experimental results have been obtained for the equilibrium at ordinary temperatures.

Under assumptions described in a previous report from these Laboratories (6) on carbonation of concrete, an approximate calculation was made for the equilibrium points in dilute solutions. The results are given in Table 1. It can be seen that the reduction in alkalinity by the presence of the carbonate is negligibly small. One would thus expect high regeneration of alkali and low solubility of carbonate under these conditions.

TABLE 1

EQUILIBRIUM CONDITIONS FOR REACTION OF CALCITE WITH ALKALI METAL HYDROXIDE SOLUTIONS

Init. Alkali Conc. (M/l)	Sol. Composition (M/l)		pH	Solid $Ca(OH)_2$
	[Ca^{++}]	[OH^-]		
0.001	14.9×10^{-5}	0.00120	11.06	Absent
0.01	11.2×10^{-5}	0.0100	11.95	Absent
0.1	17.1×10^{-5}	0.100	12.88	Absent
1.0	15.5×10^{-5}	0.999	13.75	Present

In more concentrated alkali solutions, two complications occur. Gaylussite or buetschliite replaces calcite as the solid phase, as reported by Newlon and Sherwood (7). In addition, the approximation used in the calculation for determining the activity coefficients from the ionic strength principle is no longer valid. Inasmuch as the solubilities of the new solid phases have not been determined, little insight can be gained by purely theoretical calculation.

A more direct type of evidence indicates that considerable alkali regeneration takes place even at high concentrations. Swenson and Gillott (8) describe an experiment in which a laboratory concrete containing expansive carbonate aggregate and high alkali cement was cured moist for 7 days and then stored at 50 percent relative humidity for 70 days. Upon immersion in water, a very rapid expansion occurred. This effect is precisely what would be expected if alkali regeneration continued, and is the opposite of the expectation if the drying promoted alkali removal by formation of a complex carbonate containing alkali.

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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.

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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 x 4.5 x 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

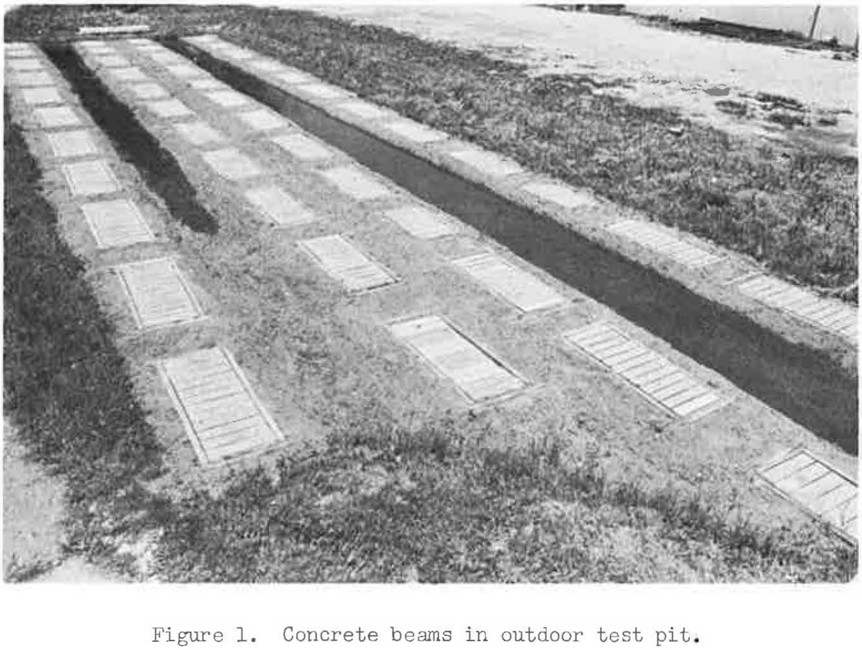

Figure 1. Concrete beams in outdoor test pit.

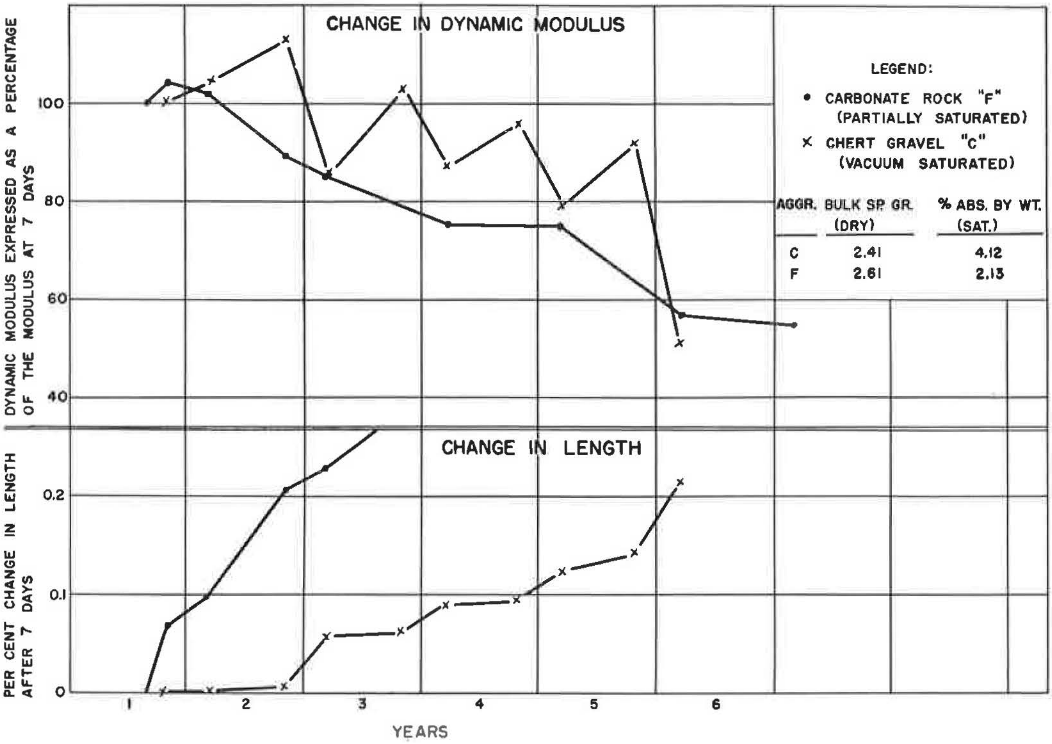

Figure 2. Normal concrete subjected to outdoor exposure.

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.

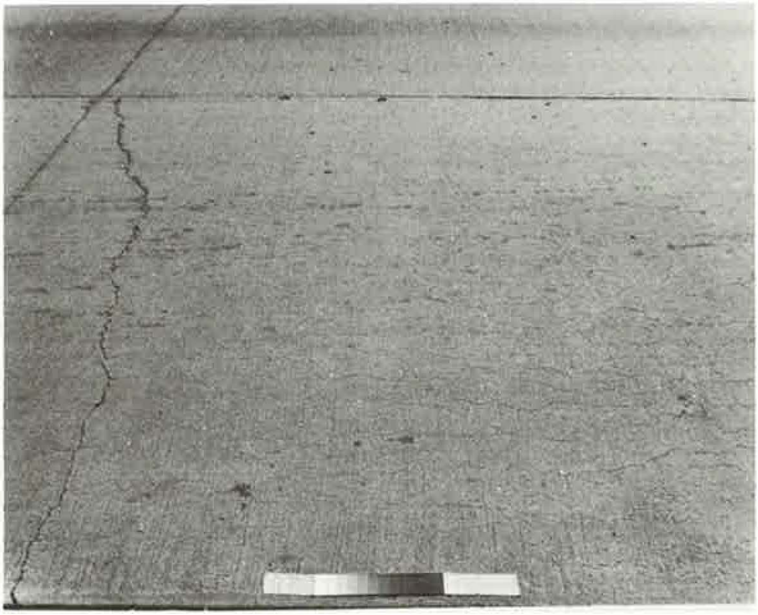

Figure 4. Cracking in PCC pavement.

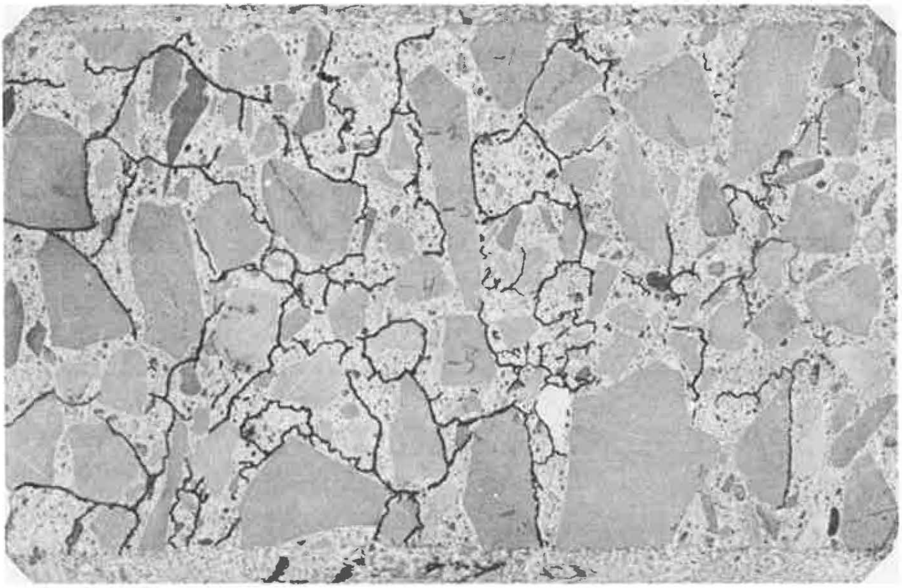

Figure 5. Microscopic cracking in PCC pavement.

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 x 5/16 x 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.

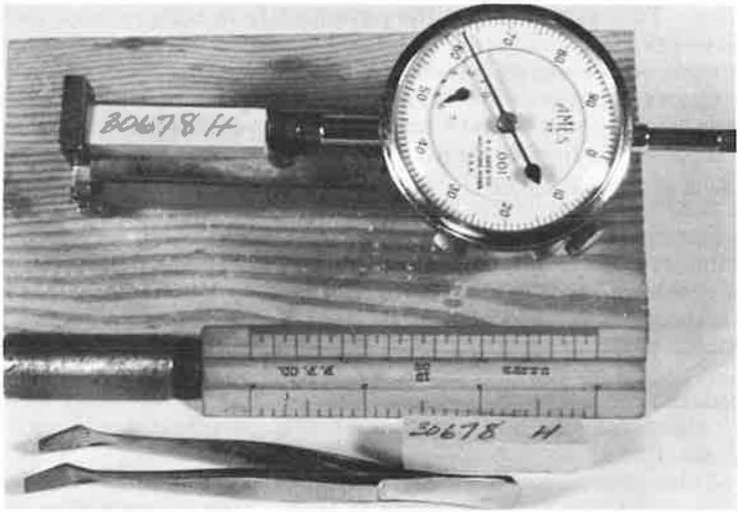

Figure 6. Comparator for measuring small rock prisms.

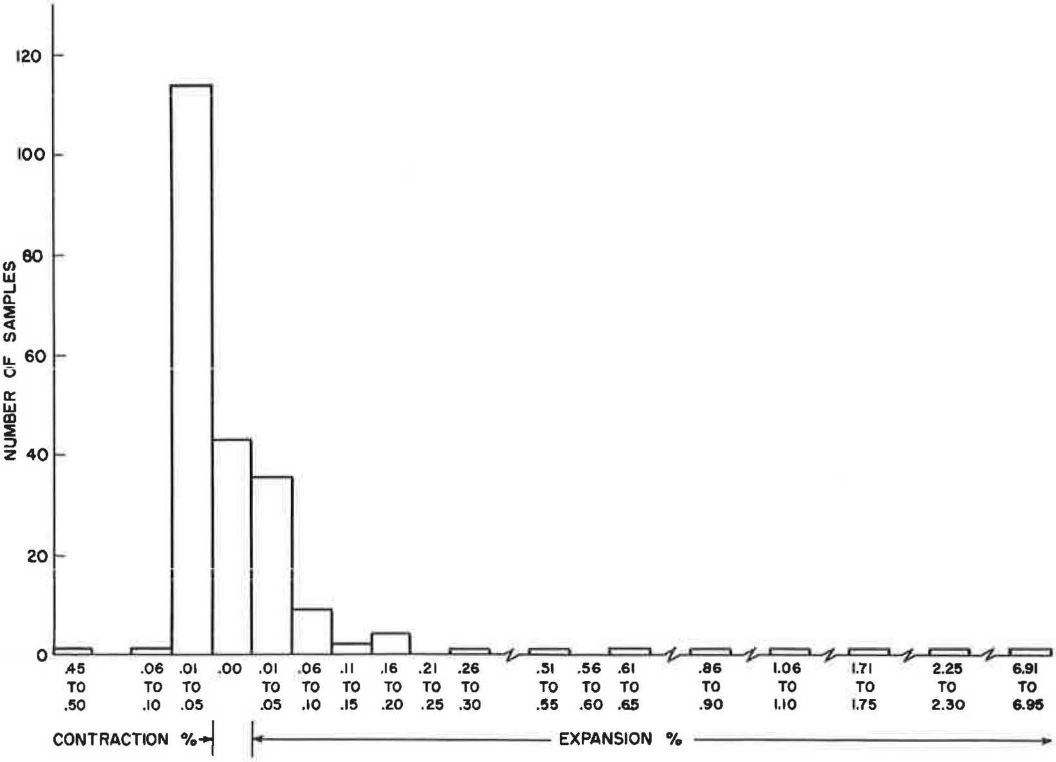

Figure 7. Distribution of prism expansions and contractions (average of two prisms perpendicular to bedding plane).

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.

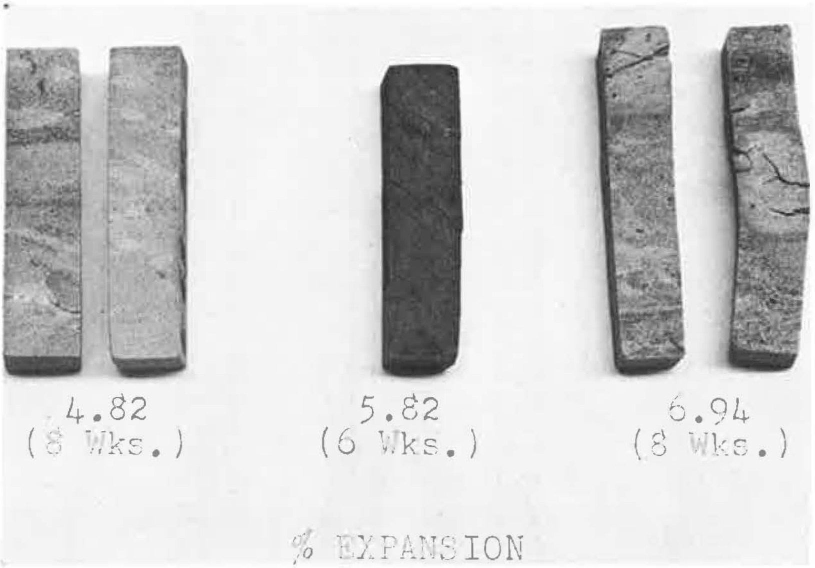

Figure 8. Three samples of prisms exhibiting high expansion.

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)

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

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

[3] Not 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 ½ 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- × 2- × 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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Learning to Live With a Reactive Carbonate Rock

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Faced with building a four-lane concrete highway for 30 miles west of Kingston, Ont., where the local dolomitic-limestone aggregates might show expansive reactivity in concrete in the presence of alkali, an investigation was made to determine the safest and most economical way of doing this. Selection of aggregates proved possible on the basis that they showed little expansion in concrete prisms made with high alkali cement and cured under standard conditions.

Confirmatory data were obtained in the laboratory on the factors that influence the degree of expansion and the effect of alkalies from a source other than the cement. Also described are precautions taken to insure that only non-reactive aggregates were used and that the other factors favoring expansion were minimized.

•WHEN serious notice was first taken in 1956-57 of the expansive reactivity of concrete in and about Kingston, Ont., the Department of Highways had almost completed the construction of the structures for part of a four-lane controlled-access highway which formed a bypass to that city. A close look at culverts and bridges constructed only a few months previously showed that there were traces already of the telltale pattern of map cracking that typified the appearance of older concrete in the area. The early observations of Swenson (1, 2) indicated that dolomitic-limestone aggregate from certain local quarries was an essential ingredient of affected concrete. It was therefore decided to import a gravel aggregate of known good performance from Brighton, 75 miles away, for the 325- by 90-ft concrete deck of the bridge over the River Cataraqui which remained to be placed. (Fortunately, considering the circumstances, a bituminous pavement had been already selected for the bypass.)

Although this was a satisfactory emergency solution to the problem, it was not a very economical one. Future plans called for the extension of the highway east and west of Kingston. Traffic, engineering, and economic considerations suggested that under normal circumstances the pavement for some 30 miles west of Kingston should be in portland cement concrete. To do this would involve concreting 24 major structures and 800,000 sq yd of 9-in. thick reinforced concrete pavement. All told, 250,000 cu yd of concrete requiring 275,000 tons of coarse aggregate would be needed. All commercially operating quarries within reach were in, or adjacent to, the Black River formation of Ordovician limestone, certain strata of which were known to be reactive. In addition, along the whole right-of-way itself, bedrock of the same suspect formation was only a few feet below ground level. Inasmuch as the extent of the reactive strata was not yet established, all working and potential aggregate sources (Fig. 1) had therefore to be regarded as suspect. The cements normally used in the area all have high alkali contents. Therefore a choice between the following alternatives was necessary.

1. Ignore the problem; switch to a bituminous pavement and import small quantities of aggregates for the concrete structures only.

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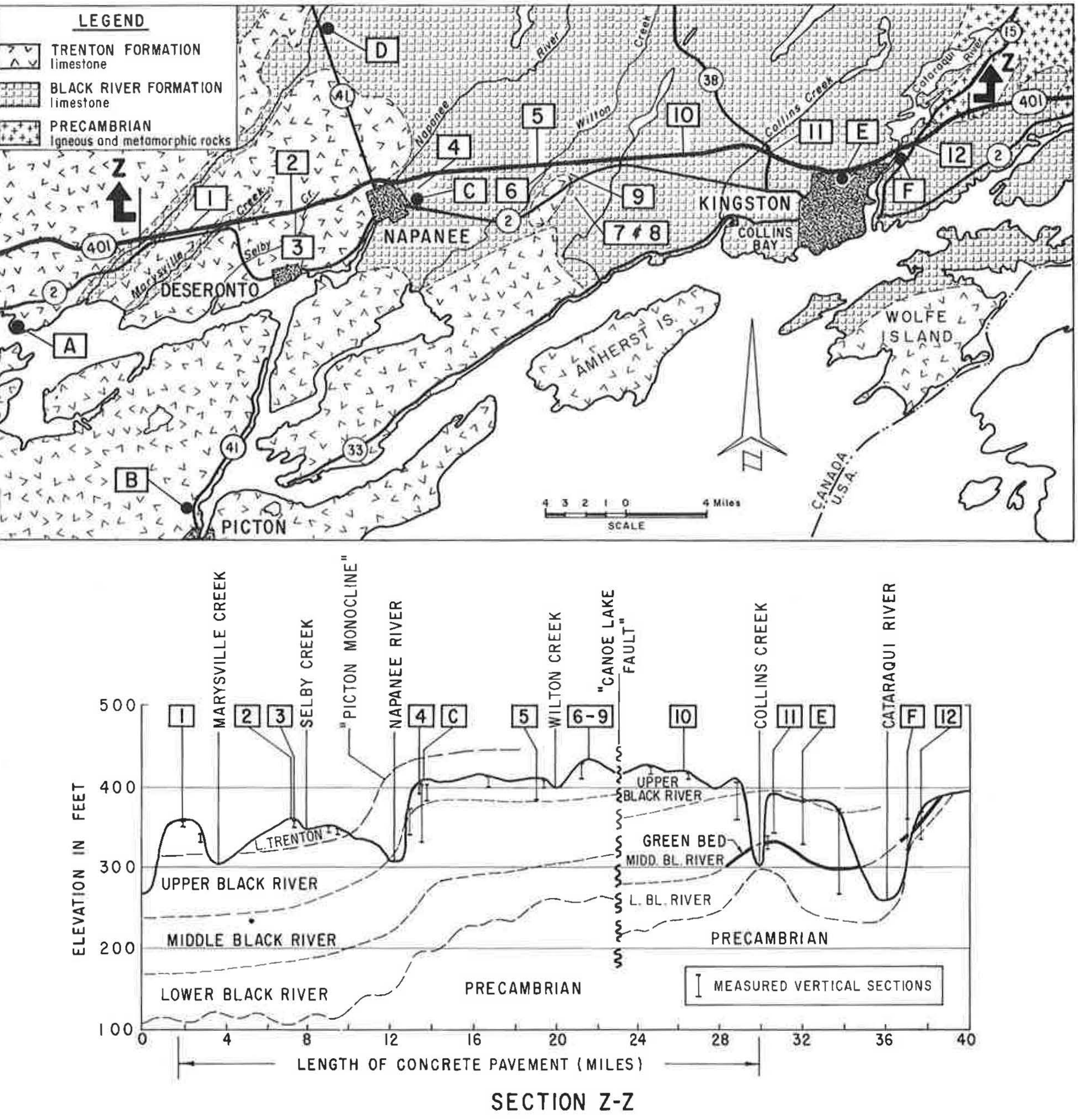

Figure 1. Highway 401, Kingston to Marysville Ont., showing geology of area and working or potential aggregate sources.

2. Import, at extra cost, large quantities of aggregate of known good quality for the concrete pavement and structures.
3. Use a low alkali cement at extra cost with any of the local dolomitic-limestone aggregates.
4. Select non-reactive local aggregates for use with the available cements of high alkali content.

This paper is concerned with the investigations that led to the adoption of the last choice, the method of aggregate selection employed and other precautionary measures which have permitted the successful and economical construction of a concrete highway through an area where previously concrete has been known to expand 6 in. in 100 ft, or to look like the bottom of a dried-out pond in summer.

FIELD SURVEY OF QUARRIES AND STRUCTURES

The commercially worked limestones of Ontario have been very thoroughly described (3). From this source and the information already accumulated in the contract records and inventory of granular deposits and aggregate sources maintained by the Department of Highways, it was possible to plan a survey to try to pin down the extent of the problem in geographical and geological terms.

The known quarries in the Kingston to Marysville area (Fig. 1) were each examined and the different strata identified. Where possible, information was gathered on how and when each quarry bed had been worked, and which structures had been built with the stone. Ledge samples of rock were secured from each different bed, together with samples of current aggregate production for subsequent examination and testing. In some quarries the whole face was being worked indiscriminately, in others the face was already benched either to facilitate quarrying operations, or because some beds were not acceptable for certain uses on the basis of usual quality tests. It was suggested to quarry operators early in the investigation that selective working might prove advantageous later on, because only certain beds, if any, were likely to be reactive.

A survey was also made of existing concrete pavements and structures, not only in the Kingston area but also over a wide part of Ontario where aggregates might have been obtained from limestones of the Trenton, Black River, Beekmantown groups of the Ordovician system. Although evidence of pattern cracking, expansion and poor durability in service was found outside the Kingston area, these could not at the time unhesitatingly be ascribed to alkali-carbonate reactivity. It was concluded from the survey that the major problem was confined to concrete containing aggregate from certain strata in the Black River formation in the Kingston area. It therefore remained to determine which beds were involved and where these were likely to outcrop as possible aggregate sources for the new highway.

IDENTIFICATION OF REACTIVE AGGREGATES

When the investigation started in 1957, the only known and certain way of detecting reactivity was to incorporate the suspect aggregates in concretes containing a cement of relatively high alkali content and measure the subsequent expansions. The test method used and the reference aggregates were essentially the same as those of Swenson and his co-workers at the National Research Council, Ottawa (1, 2, 4). This allowed a direct comparison to be made with their results throughout the investigation.

For each rock or aggregate under test, 3- x 4- x 16-in. concrete prisms were made with the aggregate at 3/4-in. maximum nominal size, standard laboratory sand, and normal portland cement with a total alkali content of approximately 1.1 percent expressed as equivalent Na_2O. The mixture was proportioned for 3,000 psi at 28 days with a fixed cement factor of 525 lb per cu yd, 3 in. slump and 6 percent air. The prisms were cured in a moist room at 70 F and 100 percent relative humidity, and length change was measured with a comparator initially at weekly and later at monthly intervals. All results are based on the average of three specimens.

From examination of the expansions of concrete containing aggregates from the working quarries surveyed, the corresponding data obtained by the National Research Coun-

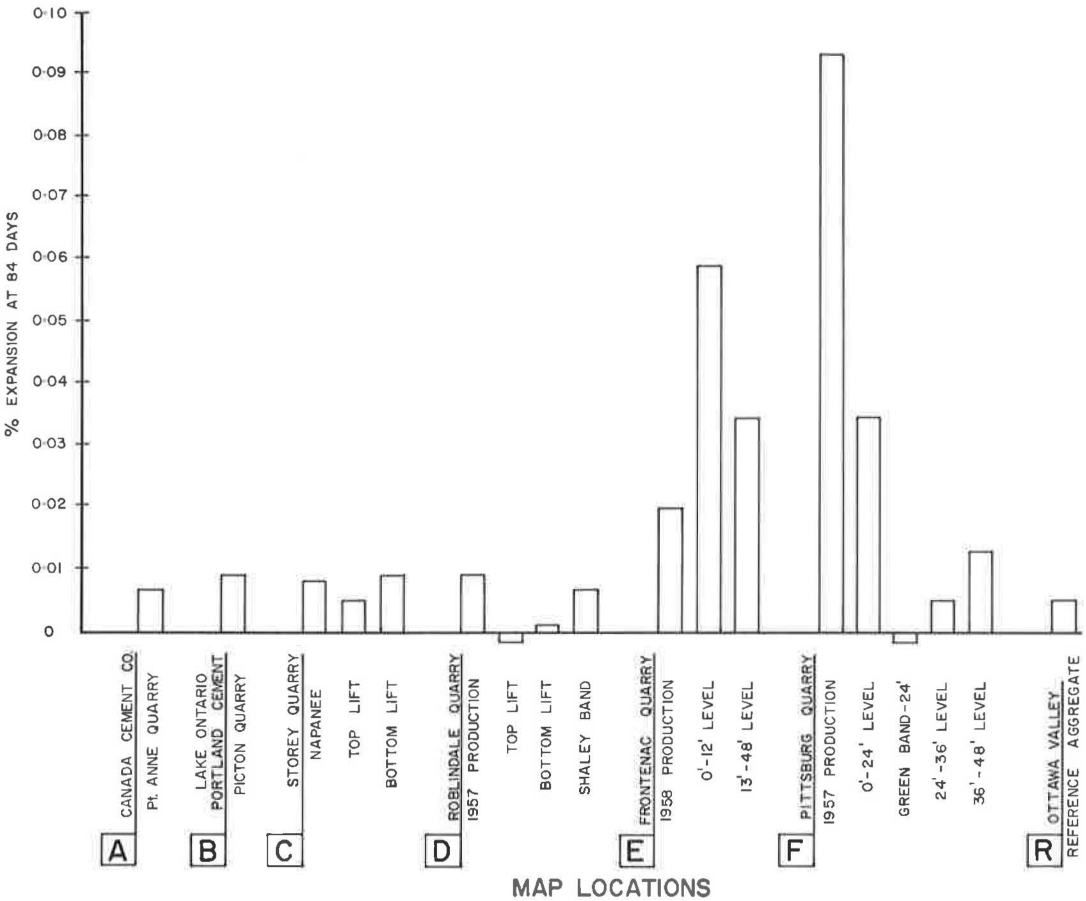

Figure 2. Expansions at 84 days of concretes containing aggregates from working quarries in Kingston to Marysville area.

cil and the field examination of structures and pavements containing aggregate from the same sources, a criterion was established that for acceptability the expansion must not exceed 0.05 percent at 84 days. (Subsequent consideration suggests that this might well be very much lower, about 0.02 percent.) The expansions at 84 days for concretes containing aggregates from the working quarries in the Kingston-Marysville area are shown in Figure 2. These indicated that the problem appeared to be limited to two quarries, Pittsburgh and Frontenac, in Kingston.

Because bedrock was at the surface along almost all the right-of-way, a contractor might well wish to open a new quarry adjacent to the highway to produce his concrete aggregates. It was obviously impractical to test every inch of the ground for alkali-carbonate aggregate reactivity during the pre-contract investigation, therefore attention was directed to those properties which had been acquired by the Department in order to obtain the right-of-way. Such potential quarry sites (Fig. 1) were core drilled, and after logging the recovered cores were subjected to testing for alkali-aggregate reactivity in addition to normal quality testing. Figure 3 shows the results of this phase of the investigation. Usually, the contracts for the concrete paving were let in the early fall for construction next year. If the contractor wished to produce aggregate from an untested location, of his own choice, it was thought that ample time was still available during the winter for testing, even though a 112-day minimum time of testing was involved.

PROBLEM OF SECONDARY ALKALIES AND POSSIBLE USE OF LOW ALKALI CEMENTS

Swenson (2, 4) and his co-workers have shown that the addition of alkali could be expected to increase the measured expansions of concrete containing reactive rocks in the same manner as if a cement of higher alkali content had been used. This appeared to be especially significant as far as a concrete pavement was concerned, inasmuch as there could be external sources of alkali present. Alkaline ground waters might reach the concrete and the use of sodium chloride as a de-icing chemical might generate additional sodium hydroxide within the concrete by reaction with the cement hydration products. To check the latter assumption, concrete prisms were immersed in a saturated salt solution at 70 F. As Figure 4 shows, greater expansions did occur in these circumstances.

Additional experiments were run with cements of different alkali contents, concretes of different compositions and under different curing conditions with aggregates from strata in the Pittsburgh quarry known to be reactive. The results bear out those of Swenson and his co-authors (2, 4) and show that other than possibly reducing the maximum size of the aggregate, the only factor capable of mitigating the expansion would be the use of a very low alkali cement. The 0.5 percent alkali content, which was the lowest in a cement then made in Ontario, did not appear to be low enough for safety. With time, prisms containing the most reactive aggregates and this cement still showed enough expansion to induce cracking.

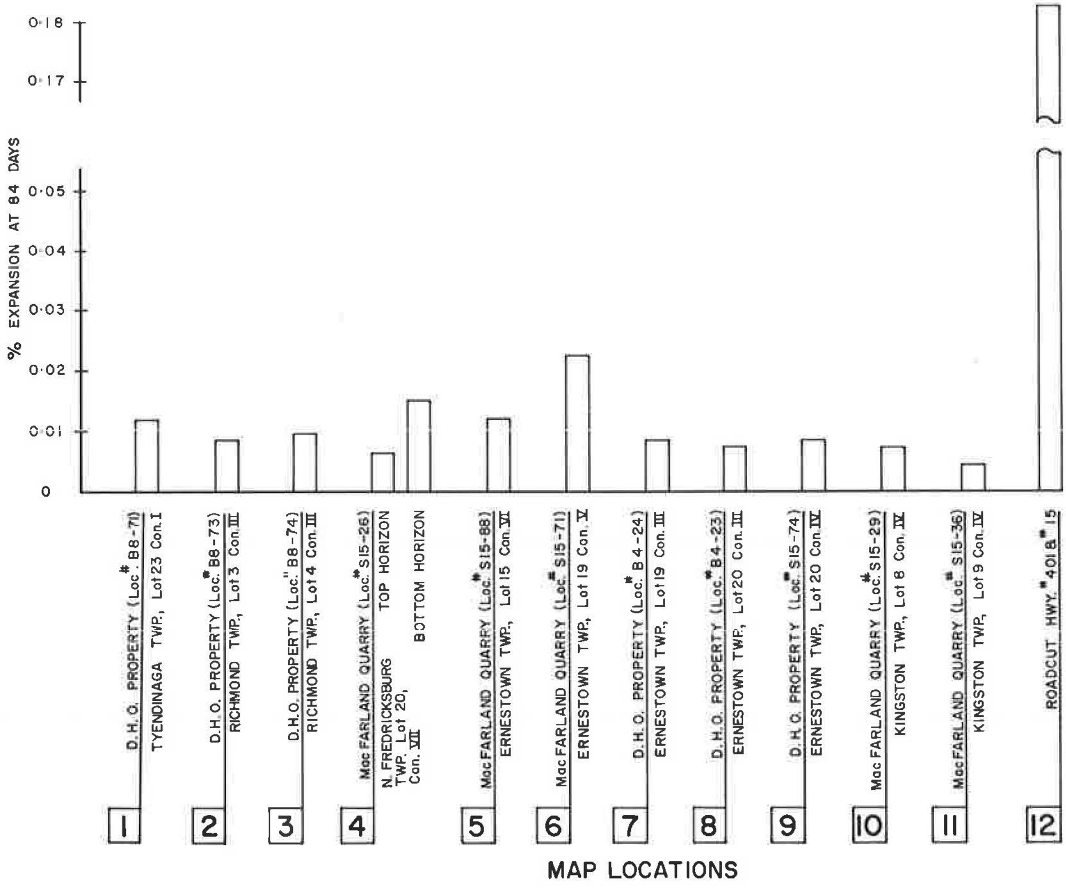

Figure 3. Expansions at 84 days of concretes containing aggregates from potential quarry sites in Kingston-Marysville area.

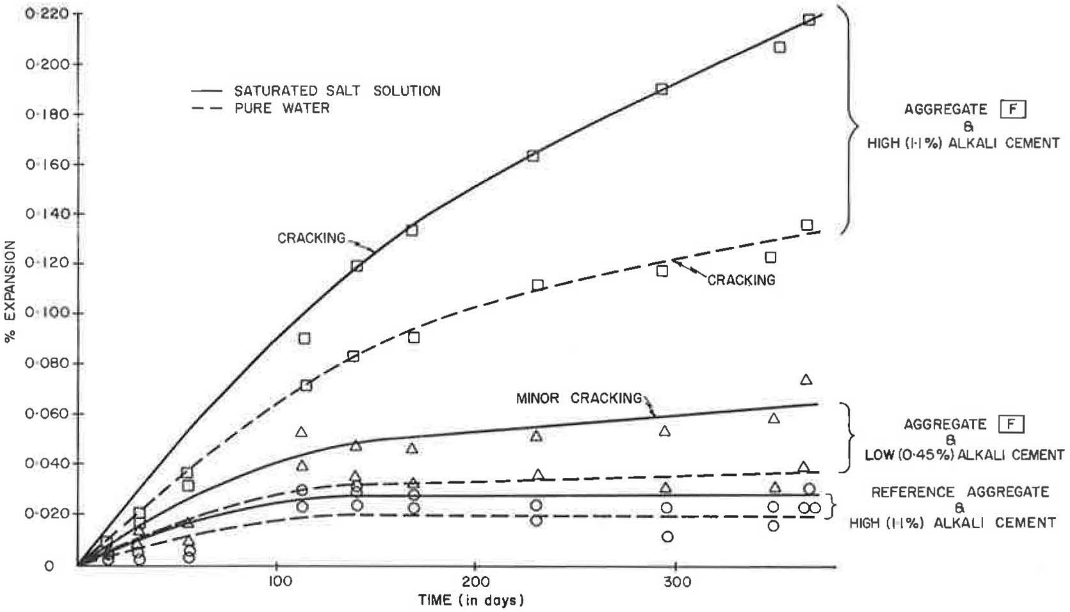

Figure 4. Effect of sodium chloride on alkali-carbonate expansive reactivity of concrete.

Considering the danger of secondary alkalies and the extra cost of the low alkali cement which would in any case be needed, it was concluded that the indiscriminate use of local dolomitic-limestone aggregates without regard for their potential reactivity was neither a safe nor an economical way to build a concrete pavement.

PRECAUTIONS SPECIFIED

As a result of the investigation, and taking into account engineering and cost considerations, it was decided to still build a concrete pavement but to use selected aggregates, while taking precautions to exclude secondary alkalies and allowing for some "warning" expansion in the pavement. Therefore, in each contract concerned, the following precautionary measures were required.

Aggregates

1. From existing commercial sources. The strata currently opened and being worked, from which acceptable non-reactive aggregates might be obtained, were designated. All unacceptable material above this had to be removed first before the acceptable material was worked, and a restriction was also placed on the production at the same time, of aggregate from reactive strata for other purposes, in order to avoid confusion and possible contamination of stockpiles.

2. Those potential quarry sites along the right-of-way which had been tested, were designated in the same manner.

3. For unworked strata in existing commercial quarries, and unexplored potential quarry sites, the contractor, if he chose to use these, was required to open the quarry to the full depth he proposed to work and permit the material to be tested prior to use.

A testing period of 112 days was specified, which included the actual expansion measuring time of 84 days. A limiting expansion of 0.05 percent was set when the aggregate in question was incorporated in a concrete prism with a cement of alkali content greater than 1.1 percent. If the contractor wished to process aggregates while waiting out the testing period, he was at liberty to do so at his own risk, provided aggregate from each different lithological sequence was separately processed and stockpiled, on the understanding that it would only be acceptable if results of the testing were satisfactory.

4. Those strata in two commercial quarries (Frontenac and Pittsburgh) known to be unacceptable together with the local deposits already known to be reactive (mainly in the Collins Bay area and east of Highway 38 and south of Highway 2 in the Kingston area (see Fig. 1)), were excluded outright from consideration as concrete aggregates.

Use of Moisture Vapor Barrier Under Pavement

Four-mil. polyethylene sheeting was specified as a moisture vapor underlay for the pavement to reduce upward migration of ground water which might be alkaline.

Provision of Expansion Joints in Pavement

Expansion joints were specified throughout the pavement, irrespective of the time of construction, instead of the customary practice of only providing these in early spring and late fall at intervals of 350 ft.

PRACTICAL RESULTS

Construction of structures on the highway started in 1959, and laying of the concrete pavement commenced in 1961. Examination of both structures and pavement so far reveals no trace of pattern cracking or excess expansions such as had been noted in earlier work only a few months after construction.

The coarse aggregates were in fact obtained from quarries C, D and 10 shown in Figure 1.

CONCLUSION

By prior geological exploration of existing and potential quarry sites and subsequently testing the different strata therein for alkali-carbonate reactivity by incorporating the rock in concrete prisms, the expansion of which was measured, it has proved possible to safely select aggregates which will be non-reactive. Taking into account the dangers of secondary alkalies and the extra cost of using low alkali cement or importing aggregate from outside, this appears to have been the most realistic and economical way to build a major concrete highway through the area of Black River dolomitic-limestones around Kingston, Ont.

Detection of reactivity by the expansion of concrete prisms is a somewhat laborious and lengthy process. Later work as reviewed by Hadley (5) on the known cases of alkali-carbonate reactivity has suggested that characteristics of the rock itself such as texture, calcite-dolomite ratio, clay minerals, and expansion of small rock prisms in alkaline solutions, may provide more rapid identification. Undoubtedly the petrologist can thus be of the greatest assistance to the engineer by examining and identifying the characteristics of rocks as to their potential reactivity. But pending greater certainty that all such cases of reactivity can be so detected, and there is now preliminary evidence that at least one reactive aggregate originating from a quarry in the Black River group in Ontario does not fit the postulated petrological pattern, the expansion of concrete prisms must remain as the ultimate criterion for aggregate acceptability where alkali-carbonate reactivity of the expansive type is suspected.

ACKNOWLEDGMENTS

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Methods for Reducing Expansion of Concrete Caused by Alkali-Carbonate Rock Reactions

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•LABORATORY studies and field experience have demonstrated that certain carbonate aggregates, commercially produced in Virginia, can react with alkalies to produce excessive expansion and, in some cases, cracking of concrete (6, 7). The Research Council's study of these reactive carbonate aggregates has been divided into several segments to facilitate conduct of the work. This paper considers the segment designed to evaluate several measures that might be employed to reduce or minimize expansion where it is in the interest of economy to use carbonate aggregates which are alkali-reactive. Other phases of the work are directed toward test methods, geologic factors, field surveys, etc., and have been or will be discussed in other papers. Although not complete, the data obtained to date are thought to be of sufficient value and interest to warrant presentation. Manifestations of the alkali-carbonate aggregate reaction, which occur as rim formation without significant expansion (4) have not been considered in this paper, but are under study in other phases of the project.

PURPOSE AND SCOPE

Measures discussed in this paper when reactive carbonate aggregates, particularly argillaceous dolomitic limestones, must be used, are: (a) reduction of the cement alkalies, and (b) dilution of the reactive aggregate with non-reactive aggregate. The benefits of the measures are evaluated in terms of their effect on volume change, resistance to freezing and thawing, and strength of concrete. The main emphasis is placed on volume change, because this is the property most significantly affected by the reaction. Resistance to freezing and thawing and strength are incidently affected as a result of excessive expansion, cracking, etc. Volume changes of the concrete are being studied for three exposure conditions: two in the laboratory and one in an outdoor test area.

One additional method (the use of mineral admixtures) is also under study but is not considered in this paper. The measures under study are applied to concretes containing two carbonate aggregates, each exhibiting a different degree of reactivity, and a diluting aggregate, which is non-reactive.

VARIABLES AND MATERIALS

Aggregates

The two carbonate aggregates studied have been discussed in an earlier paper (6). One, designated as 1-8, has been shown to be highly reactive to cement alkalies. The second, referred to in this paper as 1-X, is a mixture of three types of moderately reactive aggregate designated in previous work as 1-4, 1-5, and 1-6. These three rock types occur in adjacent beds, although differing in mineralogy, they are extremely similar in hand samples, making it highly impractical to separate them. On the basis of their occurrence in the quarry face, the sample should be predominantly 1-6. Because the primary parameter of concern is expansion and the expansion values are of the same order of magnitude, it was appropriate to consider the aggregate as a single entity.

Paper sponsored by Committee on Performance of Concrete—Chemical Aspects.

TABLE 1

COARSE AGGREGATE CHARACTERISTICS
(Values Except for Specific Gravity Shown in Percent)

Property	1-8	1-X			Granite
		1-4	1-5	1-6	
Bulk specific gravity (ssd)[1]	2.74	2.75	2.71	2.72	2.80
Absorption (24 hr)[1]	0.32	0.10	0.10	0.10	0.50
Dolomite/total carbonate[2]	63	<8	28	52	-
Acid-insoluble residue[3]	28	16	26	8	-
Rock prism expansion:[4]					
8 weeks	+0.69	+0.20	0.00	+0.12	-0.01
6 months	+0.95	+0.39	+0.10	+0.30	-
Soundness ($MgSO_4$ - 5 cycles) loss[5]	5.59	3.10	2.54	1.50	0.70

[1] ASTM C 127-59.
[2] X-ray method developed by Tennet and Berger (12).
[3] Residue remaining after treatment with excess HCl.
[4] For prisms, stored and tested by the method described by Hadley (2).
[5] ASTM C 88-61T.

The non-reactive aggregate used as a diluent was a granite-gneiss. Prisms cut from this aggregate showed no expansive tendency and, inasmuch as no known reaction would be expected, it was assumed that concrete containing this aggregate would exhibit "normal" behavior. In all mixtures the fine aggregate was a natural siliceous sand of proven service record. Significant characteristics of the coarse aggregates are given in Table 1.

Because these rock types have been previously discussed in detail, further discussion here is not warranted. The carbonate samples were prepared from large quantities of ledge rock, hand-picked from a commercial quarry, to represent the desired type and crushed to the proper sizes in a Virginia Department of Highways' plant. For all mixtures the test aggregates, as well as the reference granite, were artificially combined to give a fineness modulus of 7.15 with the grading given in Table 2. This grading is slightly coarser than normally would be acceptable for structural concrete used in Virginia, but it was adopted because it would best utilize the materials available.

Cement Alkalies

The effect of using cements of different alkali contents has been evaluated using four cements with alkali contents, expressed as equivalent Na_2O, of 0.95, 0.57, 0.43, and 0.19 percent. In this paper these will be designated as high, medium-high, medium-low and low. It should be noted that the medium-high cement represents the accepted limit of 0.6 percent used to specify low alkali cement for use with reactive aggregates. The complete chemical analyses are given in Table 3.

Dilution of Test Aggregates

The two carbonate aggregates were diluted in each size fraction with the granite to give percentage of 0, 25, 50, 75, or 100, expressed as a fraction of the

TABLE 2

GRADING OF AGGREGATES USED IN STUDY

Sieve Size	Cumulative Percent Retained
1 in.	0
$^3/_4$ in.	20
$^3/_8$ in.	95
No. 4	100

TABLE 3

ANALYSES OF CEMENTS

Determination	Sample Analysis (%)			
	High	Med.-High	Med.-Low	Low[1]
SiO_2	21.76	21.42	22.66	21.50
Al_2O_3	4.68	5.70	3.83	5.00
Fe_2O_3	2.48	1.94	2.95	3.40
CaO	63.46	65.35	66.36	63.20
MgO	2.51	1.71	2.18	2.40
SO_3	2.67	2.40	2.00	2.30
Ig. loss	1.52	0.62	1.79	2.00
Na_2O	0.32	0.19	0.07	0.08
K_2O	0.96	0.58	0.55	0.17
Na_2O, equiv.	0.95	0.57	0.43	0.19
Calculated compounds:				
C_3S	50.3	47.8	50.0	48.8
C_2S	24.5	25.4	27.3	24.9
C_3A	8.2	11.8	5.0	7.5
C_4AF	7.6	5.9	9.0	10.3

[1] A blend of two brands. The analysis represents a composite sample.

total coarse aggregates. Throughout the remainder of this paper references will be made in terms of "dilution"; zero meaning all test aggregate and 100 percent designating the reference granite. Dilution of a reactive aggregate would be a practical remedy in many cases because many quarries in Virginia and elsewhere, and particularly the one which supplies aggregate 1-8, contain a variety of carbonate types.

Although the effect of dilution would appear to be obvious, research with the alkali-silica reaction has shown that the expansion is not a direct function of the amount of reactive constituent but in some cases actually increases as the reactive component decreases (5).

Mineral Admixtures

Certain pozzolans have been shown to be effective in reducing expansion accompanying alkali-silica reaction (8). Preliminary indications are that similar but less beneficial results might be obtained from the use of these admixtures in concrete containing reactive carbonate aggregates (11). Two such admixtures are being evaluated under this program, fly ash and a finely ground silica flour. Both are available in the areas of Virginia in which reactive carbonate aggregates might be encountered. This phase of the project is in progress and is not discussed further in this paper.

Exposure Conditions

Because of drying shrinkage, the rate of expansion of concrete containing reactive aggregates in the field might be considerably reduced where continuously moist conditions do not prevail. The reduction of volume change, however, does not necessarily reduce the stresses in the paste due to the combined effects of expansion and shrinkage, both of which create tensile stresses. To evaluate these effects, volume changes of the concrete are being studied for three exposure conditions: (a) continuous moist storage at 73°F and 100% R. H., (b) 14 days of standard moist curing followed by storage at 73°F and 50% R. H., and (c) 14 days of standard moist curing followed by exposure in an outdoor test area adjacent to USWB Climatological Station Charlottesville 1W.

Specimens in the outdoor test plot are stored on racks which allow air circulation on all sides. Length measurements are made at three-month intervals. At each time of measurement, the specimens are conditioned for 48 hr at 73°F and 100% R. H.

These three exposure conditions will be designated in this paper as moist, dry, and outdoor. Beams for freezing and thawing tests and tensile strength cylinders were stored in the moist room until time for testing, 14 days and 6 months, respectively.

Proportioning and Handling of Materials

All concrete was air entrained and was proportioned to give the nominal values indicated in Table 4.

Sufficient concrete was made in a single batch to give three concrete beams 4 x 4 x 11 in. for volume change measurement in accordance with ASTM C157-60T, one beam 3 x 4 x 16 in. for freezing and thawing tests, and one cylinder for determinations of tensile strength by splitting in accordance with ASTM C496-62T. For each combination of the variables three duplicate batches were made, which gave nine volume change, three freezing and thawing, and three strength specimens. Three volume change beams, one from each batch, were stored in each storage condition. The three freezing-thawing specimens were moist cured for 14 days before testing in accordance with ASTM C291-61T "Resistance of Concrete Specimens to Rapid Freezing in Air and Thawing in Water." The three strength specimens were tested at the age of six months. Thus each of the specimens was from a different laboratory batch, but the results indicate that the overall coefficients of variation were within acceptable limits.

TABLE 4

NOMINAL MIXTURE PROPORTIONS

Item	Value
Cement content (bags/cu yd)	6.25
W/C, by wt.	0.50
Air content (%)	5.0
Slump (in.)	2.0
Cement-sand-coarse aggregate ratio[1]	1.0: 2.0: 3.0

[1] Varies slightly with dilution and specific gravity.

The aggregates were conditioned by soaking for 24 hours and draining for 72. This brought them to a saturated-surface-dry condition at the time of incorporation into the mix. The time of mixing was 5 min, in accordance with standard laboratory procedure. Unless otherwise noted, all procedures were in accordance with the applicable ASTM method. These procedures resulted in 120 concrete batches that were made in random order over a three-month period. The important characteristics of these concretes are summarized in Table 5. The average values and confidence limits at the 95 percent level are included for the mixes representing a given combination of variables. The amount of air entrained with the low cement was somewhat lower than that for mixes containing the other cements.

CRITERIA FOR EVALUATION OF RESULTS

Of the concrete properties under study the principal emphasis will be placed on volume change characteristics. In interpreting the results of the various volume change measurements, it is well to bear in mind that ASTM C157 is employed primarily as a measure of drying shrinkage and published test data for continuously moist-cured specimens are not extensive. Troxell and Davis (14) indicate a one-year expansion of moist-cured mortar of 0.02 percent. The absolute expansion values at one year of concrete containing the reference aggregate ranged from 0.030 to 0.036 percent and were somewhat higher than were anticipated; however, these length changes are regarded as normal. Because the primary concern of this study is the abnormal length changes resulting from cement-aggregate reaction, the data will be evaluated on the basis of the

TABLE 5

CHARACTERISTICS OF TEST CONCRETES

Combination		Cement Content[1] (bags/cu yd)	W/C[1], by Wt.	Slump (in.)	Air Content (%)
Cement	Aggregate				
H	1-8	6.34 ± 0.09	0.50 ± 0.03	1.9 ± 0.7	4.5 ± 0.6
M-H	1-8	6.34 ± 0.10	0.48 ± 0.09	1.9 ± 0.6	5.2 ± 0.6
M-L	1-8	6.33 ± 0.03	0.49 ± 0.02	2.1 ± 0.3	5.3 ± 0.5
L	1-8	6.45 ± 0.03	0.48 ± 0.01	2.0 ± 0.4	3.6 ± 0.4
H	1-X	6.34 ± 0.04	0.50 ± 0.01	1.9 ± 0.3	4.8 ± 0.5
M-H	1-X	6.35 ± 0.02	0.50 ± 0.02	1.9 ± 0.3	5.1 ± 0.5
M-L	1-X	6.31 ± 0.05	0.48 ± 0.03	2.2 ± 0.4	5.6 ± 0.4
L	1-X	6.44 ± 0.13	0.49 ± 0.01	2.1 ± 0.3	3.8 ± 0.5
H	G	6.38 ± 0.03	0.49 ± 0.01	1.8 ± 0.3	4.6 ± 0.4
M-H	G	6.36 ± 0.03	0.49 ± 0.01	2.1 ± 0.1	4.9 ± 0.6
M-L	G	6.33 ± 0.02	0.49 ± 0.01	2.3 ± 0.4	5.4 ± 0.4
L	G	6.39 ± 0.15	0.48 ± 0.01	2.0 ± 0.2	3.7 ± 0.4

[1] Calculated.

excess expansion of the concrete containing the test aggregate over that of the concrete made with the reference aggregate.

Research on alkali-carbonate reaction has not developed to a degree which will allow the establishment of absolute limits at which expansion of the test specimens can be considered indicative of adverse performance. Thus it is necessary to utilize the best information available to estimate the degree of potential distress.

ACI Committee 201 (ACI - 1962) suggests that"... for the time being materials (concrete) having linear expansions in excess of 0.03 to 0.04 greater than the (concrete containing) comparison aggregate at ages up to 10 months, should be regarded with suspicion."

For the Kingston aggregate, shown by experience to be deleteriously reactive, Swenson (11) showed linear expansions of approximately 0.20 and 0.10 percent, respectively, for moist and outdoor exposures of concrete made with cement having an alkali content of 1.19 percent (Na_2O equivalent). Smith (10) states a criterion established by the Ontario Department of Highways that for acceptance the expansion of concrete at 84 days of continuous moist storage shall not exceed 0.05 percent.

Because the aggregate expansion, freezing and thawing, and drying shrinkage would have an additive effect on the tensile stresses in the paste and because these stresses would less likely be relieved through creep in the outdoor exposure, a lower value of acceptable expansion would seem appropriate to the outdoor specimens than that applied to specimens stored continuously moist.

In evaluating the data of this paper, it is assumed that for concrete stored continuously moist, expansions of 0.03 percentage points greater than those of the corresponding reference concrete are undesirable. For specimens stored outdoors, the corresponding acceptable limit is taken as 0.02 percentage points.

RESULTS

Volume Changes

Rock Reactivity and Cement Alkali Content.--The results of volume change determinations for concrete containing the test aggregates without dilution and continuously moist cured are presented in Figures 1 and 2. Each point is the difference, or excess expansion, between the averages of three specimens, one each from the replicate batches, representing both the test concrete and the reference concrete. A summary of the absolute expansion values is given in the Appendix.

From the data presented in Figure 1 for concretes containing aggregate 1-8, which showed a high expansion in the rock prism test, it is obvious that an abnormal expansion which is a function of the cement alkali content is taking place. The data in Figure 2 indicate that a similar although much reduced expansion is taking place with the less reactive carbonate aggregate, 1-X.

For the highly reactive aggregate, 1-8, an excess expansion greater than 0.03 percent has occurred at one year with all of the cements except the low one. The time necessary to reach the limit depends on the alkali content, but a relatively rapid reaction in each case is apparent.

It is obvious that the degree of rock reactivity as well as the cement alkali content is quite important. The influence of rock reactivity can be roughly evaluated by comparing the expansions of concretes containing the two test aggregates. The very low values of excess expansion obtained with aggregate 1-X are reflected in excessively high ratios when these expansions are used as a reference. Because of this, the discussion of rock reactivity will be made on the basis of absolute expansion values rather than the excess expansion values used throughout the paper.

If it were possible to consume completely the "reactive potential" of the rock, the reaction would cease and, on the basis of the prism expansions given in Table 1, the ratio of expansions of concrete containing aggregate 1-8 to that made with 1-X would be expected to be approximately 3:1. In addition, concrete containing aggregate 1-X would be expected to expand slightly more than the non-reactive reference concrete. Table 6 gives the ratios of expansion of the test concrete with aggregate 1-8 to that with 1-X and for the concrete with 1-X to the reference concrete. These ratios were computed from the absolute values of the expansions for the three concretes.

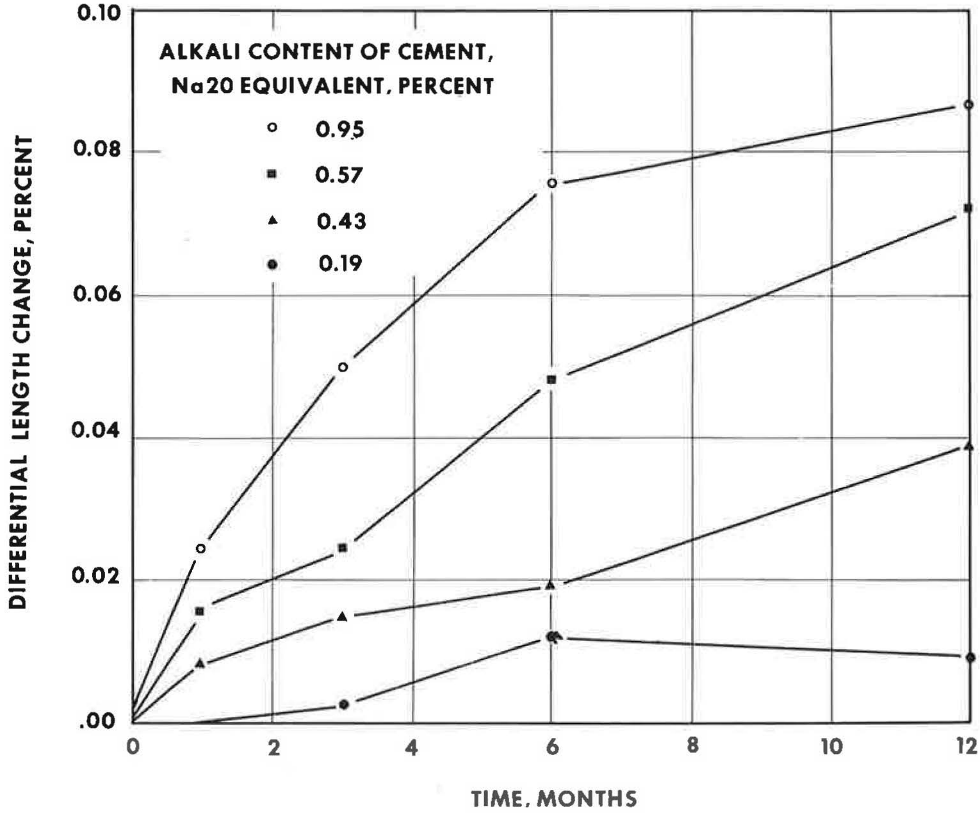

Figure 1. Excess length changes of 4- × 4- × 11-in. concrete prisms containing test aggregate 1-8 undiluted, continuously moist cured (73° F, 100% R. H.).

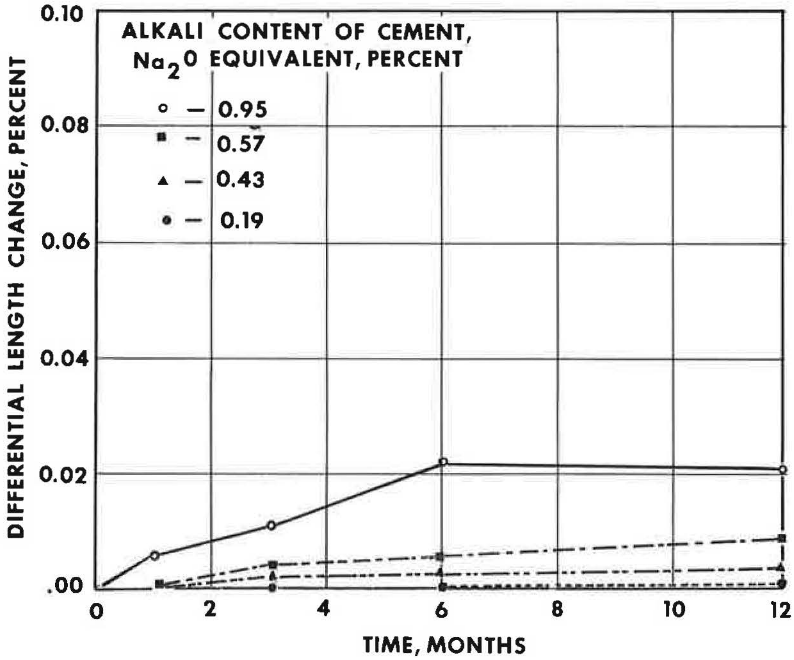

Figure 2. Excess length changes of 4- × 4- × 11-in. concrete prisms containing test aggregate 1-X undiluted, continuously moist cured (73° F, 100% R. H.).

TABLE 6

RATIOS OF EXPANSION OF TEST AND REFERENCE CONCRETES

Cement	Ratio, Conc. with Agg. 1-8 / Conc. with Agg. 1-X				Ratio, Conc. with Agg. 1-X / Conc. with Ref. Granite			
	1 Mo	3 Mo	6 Mo	1 Yr	1 Mo	3 Mo	6 Mo	1 Yr
High	2.5	2.9	2.8	2.2	2.0	2.1	3.7	1.6
Medium-high	3.0	2.4	2.6	2.4	1.0	1.2	1.3	1.2
Medium-low	2.2	2.4	1.8	2.1	1.7	1.1	1.1	1.1
Low	0.8	1.3	2.1	1.3	1.0	1.0	1.0	1.0

The results are as would be expected in that the ratios between expansions of concrete containing aggregate 1-8 and those of concrete containing 1-X are larger than those between the concrete with 1-X and the reference concrete. With the higher alkali cements the ratios approximate rather well the expected value of 3 and the ratios are relatively constant with time.

Where the aggregate is reactive, the expansion is directly related to the cement alkali content. To achieve a given level of expansion requires a longer time with the lower alkali cements but, except for the lowest alkali content tested, an undesirable expansion is indicated when aggregate 1-8 is used undiluted, and the expansions appear to be continuing.

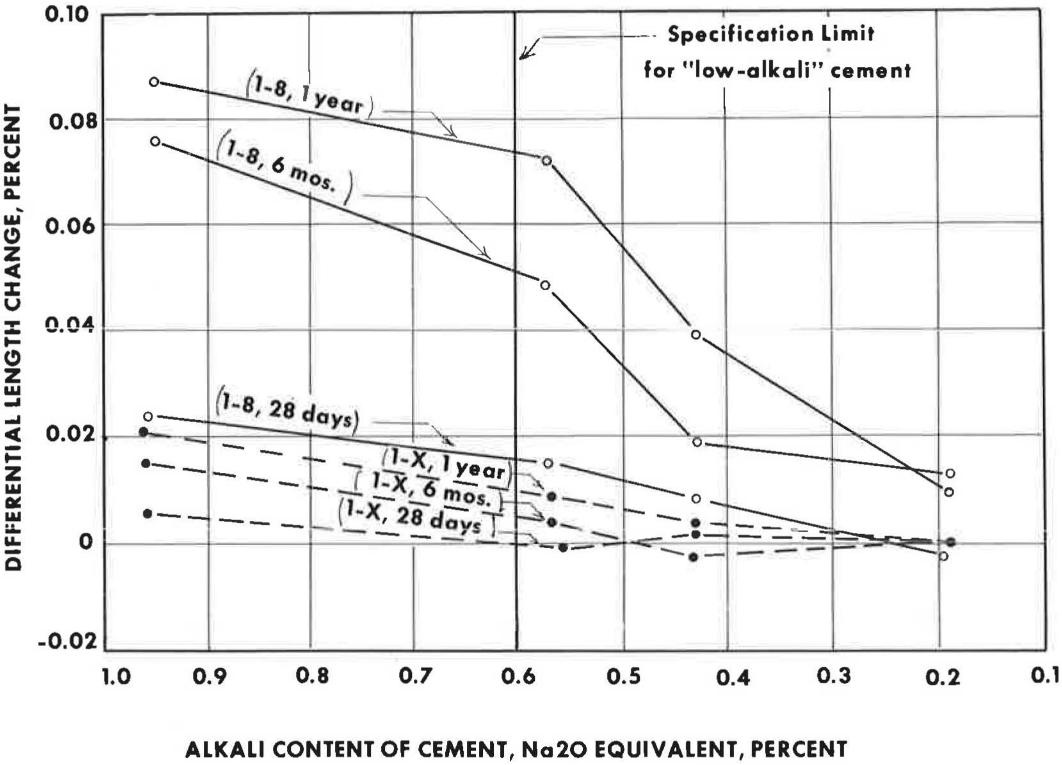

Figure 3. Effect of cement alkali on expansion of continuously moist-cured concretes containing the test aggregates.

The effect of alkali content on the expansions of the moist-cured concretes containing both undiluted test aggregates is summarized in Figure 3, which gives the data for expansions in excess of those of the corresponding reference concretes at 28 days, six months, and one year. The effect of reduction of alkali content appears to be more pronounced below 0. 6 percent than above this value.

For the data shown in Figure 1, which gives the results of tests with concrete containing aggregate 1-8, the ratio of excess expansions at one year for the three highest alkali cements is 2. 2: 1. 8: 1. 0, whereas the ratio of the alkalies is 2. 2: 1. 3: 1. 0. Somewhat higher ratios are obtained for aggregate 1-8 if the low cement is taken as a base. The same is true in all cases involving aggregate 1-X. This results from the fact that the reaction in these cases is very small. Thus, for the most reactive rock, a good correlation of the ratio of expansions at one year with the ratio of the alkali contents is found if the medium-low cement is taken as a base. It is of interest to note that for aggregate 1-8 and all cements, the excess expansion is essentially the same at an age of 28 days as is that for aggregate 1-X at an age of one year.

With aggregate 1-8, the medium-high cement with an alkali content of 0. 57 percent, which would be a low-alkali cement as designated by current ASTM specifications, has resulted in undesirable expansion at four months. Reduction of the cement alkalies to 0. 43 percent also has provided only temporary relief. In no case has the concrete with aggregate 1-X shown undesirable expansion although some significant expansion is indicated with the high cement.

The data indicate that the generally accepted specification value of 0. 6 percent for low alkali cement is not sufficiently restrictive with aggregates similar to 1-8[1]. On the basis of these laboratory tests, it appears that the limit should be 0. 4 percent or less, although this limit might be too severe for field concrete in which some drying is possible, and would depend on the amount of reactive material present, as discussed later in this paper.

On the basis of field evidence reported in an earlier publication (6), structures containing aggregate 1-8 diluted by approximately 50 percent, and a cement similar to the medium-low cement reported here, exhibited borderline performance.

Thus, for aggregate 1-8, used undiluted, control of the expansion by reduction of the cement alkalies alone does not seem practical. The interaction of alkali reduction with other factors is discussed later in this paper.

The data further indicate that aggregate 1-X, even in the most unfavorable combinations, would develop excessive expansion only after very long exposure to the continuously moist environment, if then. Thus it appears that the degree of rock reactivity is of considerable importance and that a mildly reactive rock can be tolerated under most field conditions.

Dilution. —The effect of dilution of the reactive aggregate component on the one-year expansions of concretes containing aggregate 1-8 is shown in Figure 4. The expansion is expressed as the differential length change between the test and reference concretes. Dilution is shown to be effective in reducing the volume change at a given age roughly in proportion to the amount of reactive material removed.

If the dilution necessary to bring the excess expansion at one year under 0. 03 percent is roughly estimated by interpolation from the curves in Figure 4, the minimum dilution for the high cement is 73 percent. The corresponding minimum dilutions for the medium-low, and low cements are 58, 30, and zero percent, respectively. The maximum excess expansion of all combinations involving test aggregate 1-X is less than 0. 03 percent.

In addition to the individual and combined effects of alkali content and dilution, the influence of time on the expansion can be seen from the data in Table 7 and Figure 5.

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[1] Attention is directed to the fact that ASTM C150-61 and AASHO M 85-60 differ in that the latter carries a note to the effect that "This requirement applies only when the engineer specifies the 'low alkali cement'. Such cement should be specified only when alkali reactive aggregates are to be used in the concrete. The maximum value of 0.6 percent may be reduced when the experience of the engineer indicates that such action is desirable." Thus the reduction of alkalies to an acceptable amount is currently permissible under AASHO M 85-60.

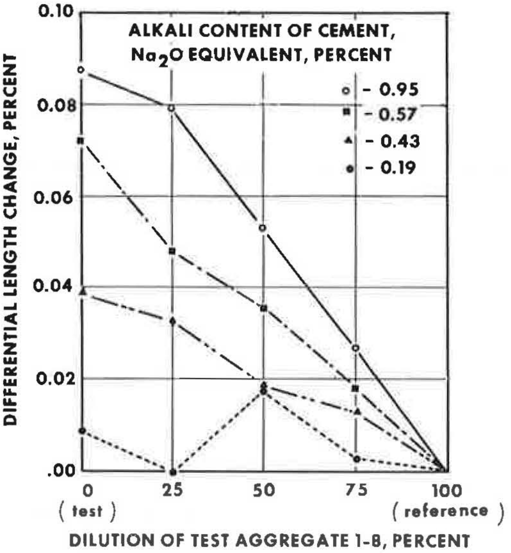

Figure 4. Effect of dilution of aggregate 1-8 on expansion at one year of concrete specimens continuously moist cured.

TABLE 7

SUMMARY OF EXPANSION DATA[1] FOR MOIST-CURED TEST CONCRETES, AGGREGATE 1-8

Cement	Dilution (%)	Excess Expansion (%)		
		3 Mo	6 Mo	1 Yr
H	0	0.050[2]	0.076[2]	0.087[2]
MH	0	0.024	0.048[2]	0.072[2]
ML	0	0.015	0.019	0.039[2]
L	0	0.002	0.012	0.009
H	25	0.053[2]	0.073[2]	0.079[2]
MH	25	0.027	0.042[2]	0.048[2]
ML	25	0.018	0.019	0.033[2]
L	25	0.002	0.010	0
H	50	0.031[2]	0.058[2]	0.053[2]
MH	50	0.015	0.029	0.036[2]
ML	50	0.009	0.019	0.016
L	50	0.010	0.034[3]	0.018
H	75	0.013	0.028	0.027
MH	75	0.006	0.012	0.018
ML	75	0.003	0.010	0.014
L	75	0	0.016	0.003

[1] Aggregate 1-X, maximum expansion at one year = 0.021 percent (zero dilution and high cement).
[2] Exceeds 0.03 percent limit.
[3] Apparent error.

As the reactive aggregate is diluted, progressively higher alkali cements can be tolerated without undesirable expansion. Likewise, for a given alkali content, the time required to reach the undesirable level of expansion is longer as the reactive component is diluted.

From the data plotted in Figure 5 it appears that for the concrete containing aggregate 1-8 most expansions are approaching maximum values at one year. The exceptions to this appear to be the medium-low cement at the two lower dilutions. Whether or not these combinations will expand further at later ages will only become clear with additional measurements, but it would appear that for dilutions of 50 percent or more the reduction in expansion is permanent.

Exposure Conditions. —Thus far in this paper and in most previously published work, observations relative to the effect of alkali content and aggregate dilution have been based largely on laboratory samples cured continuously moist. As previously noted, the influence of exposure conditions was evaluated for moist, dry, and outdoor environments. The behavior of the laboratory specimens exposed to the moist and dry environments was as expected (Fig. 6). It is apparent that the difference between the lengths of corresponding specimens represents a considerable potential stress. Plots similar to Figure 6 are obtained for concretes containing the other test aggregates and the reference aggregate. Concrete containing aggregate 1-8 showed approximately 50 percent greater shrinkage at one year than did that with the other two aggregates.

The need for outdoor exposure tests to supplement more rapid laboratory tests has been clearly demonstrated. As noted previously, after 14 days of standard moist curing, a specimen from each batch was placed in the outdoor exposure on wooden racks which permitted the free circulation of air. At specified intervals, the samples were brought into the laboratory and conditioned in the moist room for 48 hours prior to the measurement.

Although the beams were put into the outdoor exposure area at different times over a period of several months, after an exposure of one year they have been subjected to essentially the same environmental conditions. It should be remembered that each of the three beams representing a given combination of variables was taken from a dif-

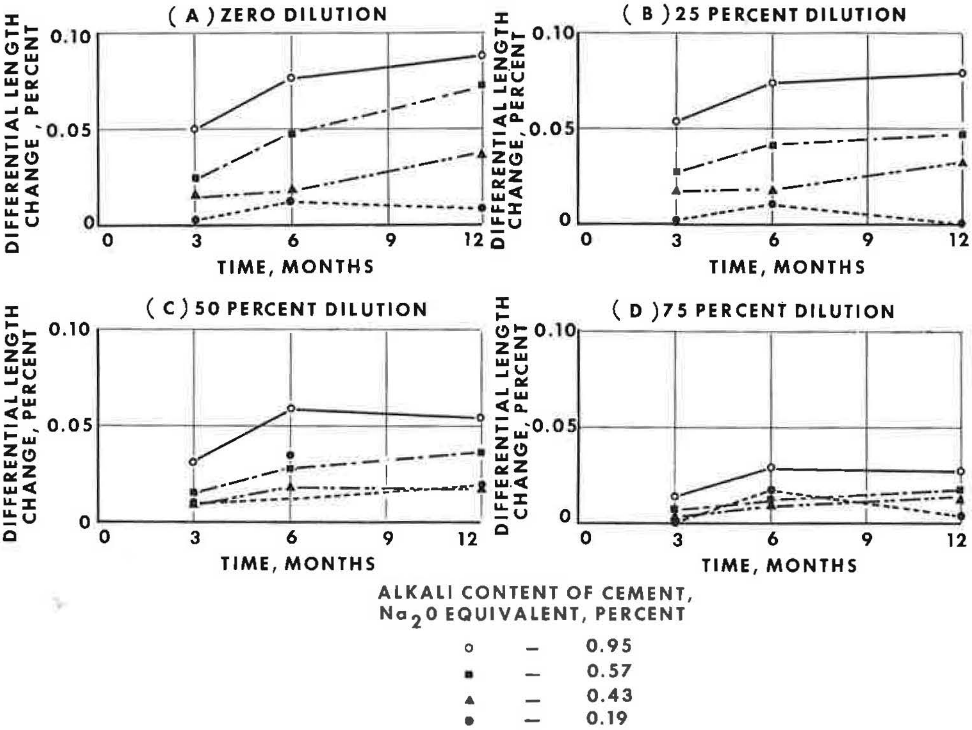

Figure 5. Effect of dilution cement alkali, and time on expansion of concrete containing aggregate 1-8 continuously moist cured.

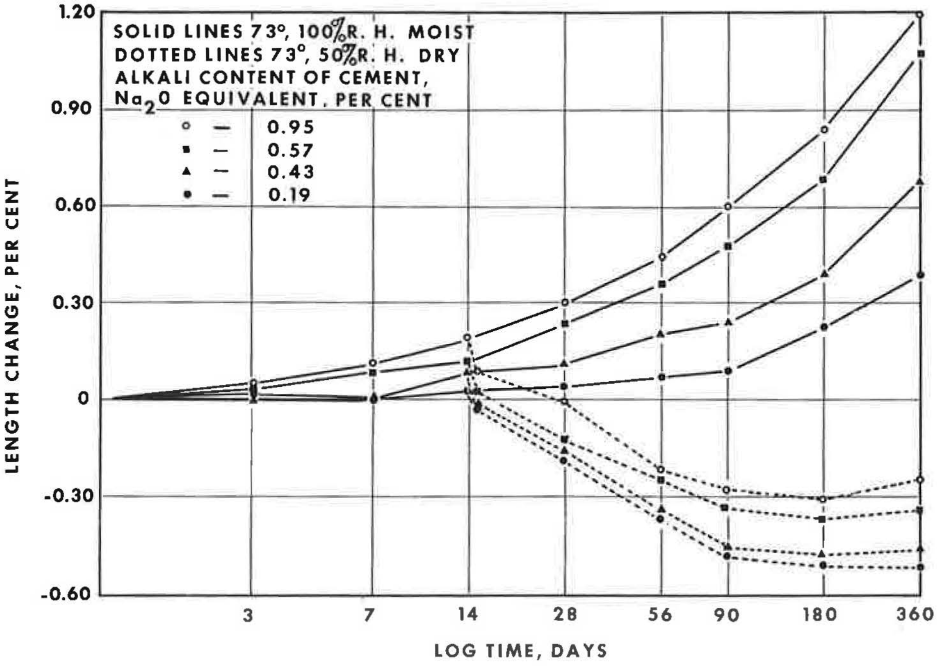

Figure 6. Length changes of laboratory concrete containing aggregate 1-8 undiluted.

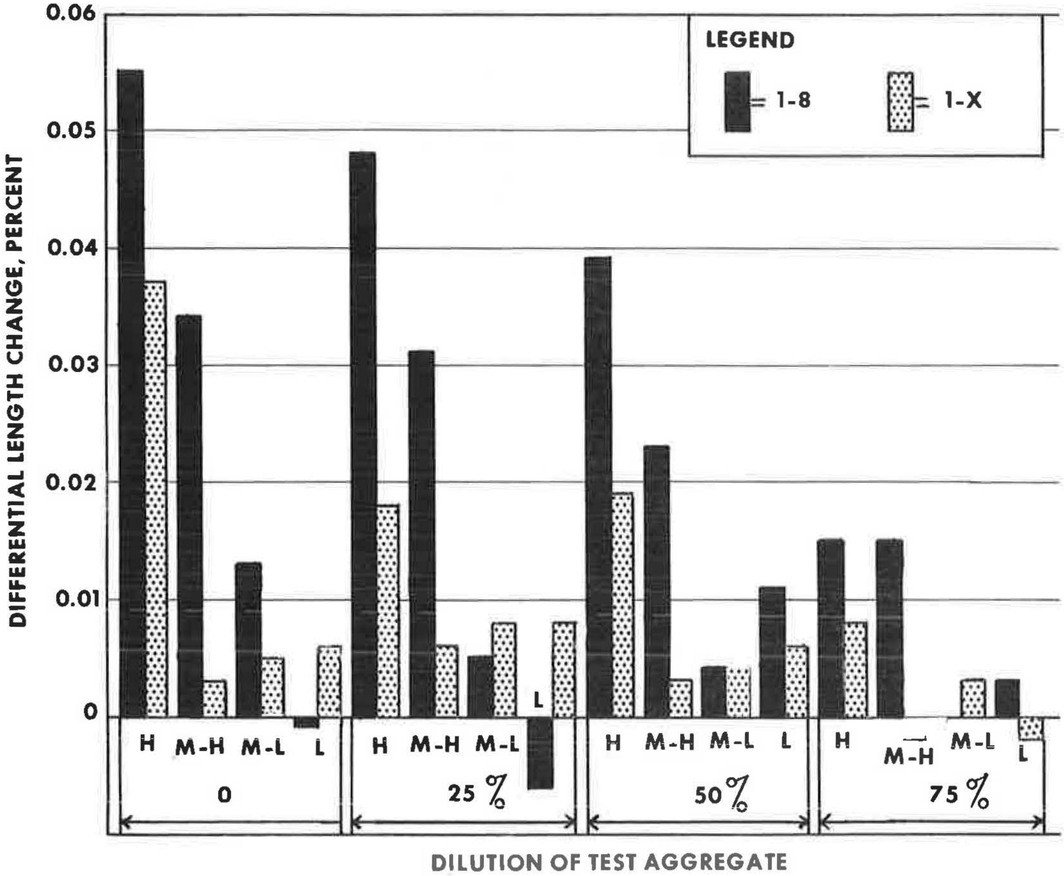

Figure 7. Effect of dilution and reduction of alkalies on the differential length change of concrete after one year of outdoor exposure.

ferent batch. Data are shown in Figure 7 for the excess length changes of concrete containing both test aggregates in all dilutions over those of the reference concrete. The values plotted are the averages of the three specimens representing a given combination. In all cases the individual values were within 0.01 percentage point of the average. Considering the fact that the specimens came from different batches and the total length changes are the result of reaction, shrinkage, and freezing and thawing, the agreement of these data is particularly good.

Applying the criterion of 0.02 percentage points excess expansion to the outdoor data, the unacceptable combinations will be seen as, (1) aggregate 1-8 with the high and medium-high cements with dilutions less than approximately 50 percent, and (2) undiluted aggregate 1-X with the high cement. By comparison of all the data presented in the Appendix, it appears that the outdoor value obtained with the high cement and aggregate 1-X is excessively high, but no reason is apparent.

If the minimum dilution of aggregate 1-8 required to achieve the 0.02 percent limit is roughly interpolated from Figure 7, it would be for the high and medium-high cement 70 percent and 60 percent, respectively. The corresponding values presented earlier from the moist specimens were 73 percent and 58 percent. The medium-low cement does not show excessive expansion outdoors at this age but perhaps will do so on longer exposure.

An interpretation of the data for the outdoor specimens is aided by comparison with those for the specimens stored continuously moist. Table 8 gives data for moist-cured specimens at ages of 90 days and one year and those for outdoor specimens at 90 days.

TABLE 8

SUMMARY OF EXPANSION VALUES FOR TEST CONCRETES IN MOIST AND OUTDOOR ENVIRONMENTS

Cement	Aggregate	Expansion, 90 Days (%)		Expansion, 1 Year (%)				Ratio of Outdoor Expansion at 1 Year to Moist Expansion at 90 Days
		Moist Storage	Excess	Moist Storage	Excess (Moist)	Outdoor	Excess (Outdoor)	
High	1-8	0.060	0.050[1]	0.120	0.087[1]	0.068	0.055[1]	1.13
High	1-X	0.021	0.011	0.054	0.021	0.050	0.037[1]	2.50
High	G	0.010	-	0.033	-	0.013	-	1.30
Medium-high	1-8	0.036	0.024	0.108	0.072[1]	0.048	0.034[1]	1.33
Medium-high	1-X	0.015	0.003	0.045	0.009	0.017	0.003	1.13
Medium-high	G	0.012	-	0.036	-	0.014	-	1.17
Medium-low	1-8	0.024	0.015	0.069	0.039[1]	0.028	0.012	1.17
Medium-low	1-X	0.010	0.001	0.033	0.003	0.020	0.004	2.00
Medium-low	G	0.009	-	0.030	-	0.016	-	1.78
Low	1-8	0.009	0.002	0.039	0.009	0.008	-0.001	0.89
Low	1-X	0.007	0	0.030	0	0.014	0.005	2.00
Low	G	0.007	-	0.030	-	0.009	-	1.28

[1] Exceeds limits of: 0.03 percent—moist, 0.02 percent—outdoor.

At one year the expansion of the outdoor specimens is approximately one-half of that for the specimens cured continuously moist. As indicated, a good estimate of the one-year length change of the outdoor specimens is obtained from the 90-day moist-cured value. With the exception of the values for 1-X and the high cement and for several combinations in which the total volume changes are very small, the 90-day moist values rather closely approximate the one-year outdoor values.

It is well recognized that this relationship probably cannot be generally applied although it does agree rather well with data presented by Swenson (11). However, it is of local interest and does lend support to the estimation of expansion from laboratory tests.

In summary, the conclusions drawn from the outdoor test support those of the laboratory and indicate that both a dilution of at least 50 percent and an alkali limit of 0.40 percent are required to limit the expansion of concrete containing aggregate 1-8 to an acceptable level.

Resistance to Freezing and Thawing

When concrete expands due to cement-aggregate interaction, tensile stresses are created in the cement paste. Similar stresses are created when concrete is subjected to alternate cycles of freezing and thawing. Inasmuch as these two effects are additive along with shrinkage stresses, it would seem that the resistance to freezing and thawing of concrete containing materials capable of alkali-aggregate reaction would be reduced as compared with that made from non-reactive materials. In order to verify this, one beam from each laboratory batch of concrete was subjected to freezing-thawing tests in accordance with ASTM C291 after 14 days of standard moist curing. This schedule resulted in the testing of three beams for each cement-aggregate-dilution combination. The results of these tests are shown in Figures 8 and 9 for the two test aggregates. The results for 100 percent dilution of the two obviously represent the resistance of the granite reference aggregate. The data shown in Figure 8 clearly demonstrate the combined effects of chemical reaction and the action of freezing. A comparison of the data shown in Figures 8 and 9 for aggregates 1-8 and 1-X indicates that the former has a lower resistance to freezing and thawing than the latter. The results of sulfate soundness tests on the materials were given in Table 1. The soundness loss of aggregate 1-8 is higher than that for the components of 1-X, but both are well within acceptable limits. The results indicate that when undiluted there is a

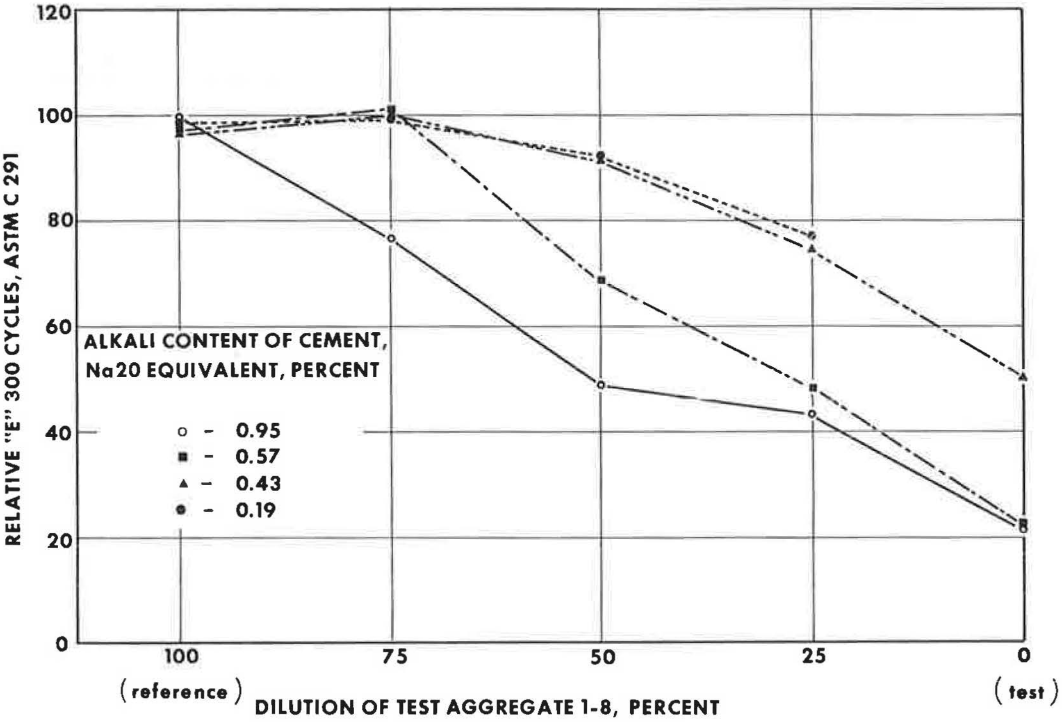

Figure 8. Resistance to freezing and thawing of concrete containing aggregate 1-8 as affected by cement alkalies (ASTM C 291).

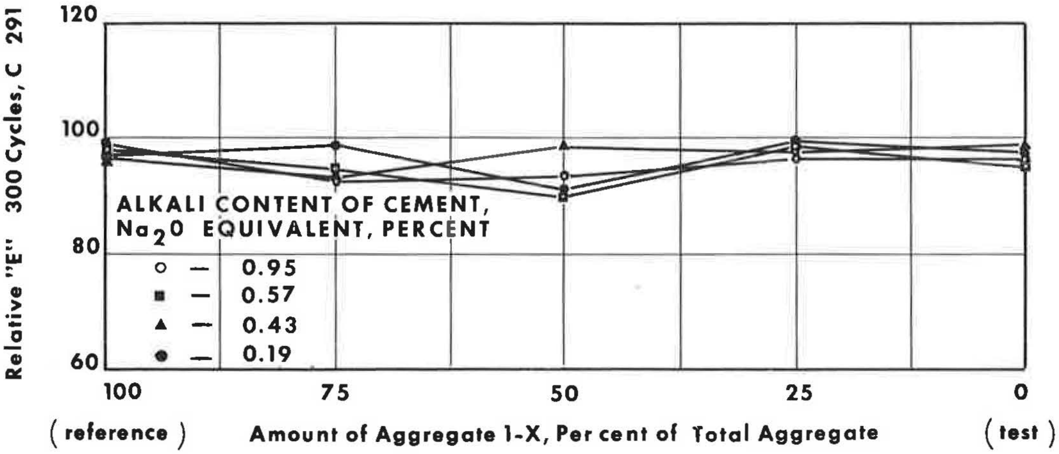

Figure 9. Resistance to freezing and thawing of concrete containing aggregate 1-X as affected by cement alkalies (ASTM C 291).

larger difference in resistance to freezing and thawing than would be indicated from the sulfate test.

Tremper (13) has reported a reduction in resistance to freezing and thawing related to cement alkalies for concrete made with aggregates showing no deleterious reaction as indicated in a mortar bar test (ASTM C227). It is not clear from his work whether or not the aggregates were deleteriously reactive, but the remedial measure which he employed successfully (entrainment of air) does not eliminate the low resistance to freezing and thawing in the present study.

As noted previously in the discussion of length changes of the beams exposed in the outdoor test area, the effect of freezing and thawing on length change cannot be separated from the effects of reaction with any degree of certainty. In fact, if the expansion is the result of a chemical reaction then it would be expected to increase with higher temperatures, whereas the expansive effects of frost action would obviously become more apparent at lower temperatures. Consequently, the two mechanisms could result in year-around expansion. Although it is probably hopeless to attempt any quantitative treatment, the beams are being evaluated in terms of exposure to freezing by means of a procedure similar to that employed by Kennedy and Mather (3) in evaluating the field exposure of concrete.

In the outdoor tests under discussion, the concrete was assumed to have frozen if the temperature fell below 28°F and to have thawed if the temperature subsequently reached 32°F. To account for the severity of prolonged periods of freezing, each cycle was multiplied by the number of degrees below 28° to give the number of "degree-cycles." The cumulative total thus represents the number and severity of the freezing cycles. One winter's exposure has not been sufficient to develop clear trends. The ranges to which the beams have been exposed are (a) cumulative cycles 63 to 70, and (b) cumulative degree-cycles 677-743. This will be recognized as a relatively severe winter. As a matter of comparison the cumulative index for the laboratory tests discussed earlier would be 8400.

Strength

Only limited data on the effects of the variables on strength have been developed. On the basis of preliminary tests involving concretes essentially like those included in the main experiment, it appeared that the tensile strength would be more sensitive to the effects of the expansive reaction than would the compressive strength. For concrete containing aggregate 1-8 in combination with the high and medium-low cements a retrogression of tensile strength as measured by the splitting test (ASTM C496) was observed as indicated in Table 9.

It appeared from these preliminary data that cracks apparently formed at an expansion of between 0.03 - 0.07 percent, and although they were not always visible, they were sufficient to reduce tensile strength. Whether the strength reduction with the medium-low cement was real or not will only be known when the one-year tests are made.

Guided by the results of this preliminary study, one cylinder was made from each of the batches in the main experiment for tensile splitting tests. This gave three specimens for each combination of variables, just as in the case of the freezing-thawing studies. All of these cylinders were tested at an age of six months after continuous moist curing. Although the strengths varied depending on the particular combination of cement and aggregate, there was no significant difference in the strengths which could be related to the expansion values or other indications of chemical reaction.

Visual Evidence of Distress

Apart from quantitative measurements which have been discussed, some indication of the various interactions and effects on overall performance can be gained from examination of the general appearance of the beams. It should be emphasized that the following observations are based on individual judgments and are thus somewhat speculative. However, it is felt that the general agreement of all laboratory and field observations to date warrant such speculation.

The only visual evidence of distress which has been noted is a very fine pattern

TABLE 9

INFLUENCE OF EXPANSION ON TENSILE SPLITTING STRENGTH

Age	High Cement		Med.-Low Cement	
	Tensile Strength (psi)	Expansion (%)	Tensile Strength (psi)	Expansion (%)
28 days	446	0.03	391	0.02
90 days	368	0.07	475	0.03
6 mo	319	0.09	388	0.04

cracking similar to that observed in cases of the alkali-silica reaction. This cracking has occurred in some of the beams containing aggregate 1-8 in combination with the higher alkali cements. Pictures of typical cracks and patterns have been given in an earlier report (6). Cracking is usually less evident in beams stored continuously moist than for those exposed out-of-doors, even though in the former case the expansions are approximately double those in the latter. Apparently the cracking observed is the result of combined tensile stresses resulting from the interaction of expansion, shrinkage, and freezing and thawing. The fact that the cracking is finer than that normally associated with alkali-silica reactions is interpreted to be a manifestation of the fact that the expansion is not produced by an "unlimited swelling gel" that can imbibe water (9), but by a reaction finitely controlled by alkali and aggregate reactivities. That relatively high expansions can be accommodated by concrete in a moist environment without visible cracking is thought to be related to the fact that the reacting aggregate is uniformly distributed throughout the beam rather than concentrated at relatively few sites, and that the stresses are relieved to some degree by creep of the moist concrete.

As a result of the tests to date it appears that the tendency toward expansion is increased by moist storage, whereas the tendency toward cracking is greater in areas where several factors combine to produce tensile stresses in the paste. This confirms the findings of previous limited field observations (6) in which it was noted that cracking was more apparent in bridge decks, handrails, etc., than in massive abutments and foundations.

CONCLUSIONS

The following conclusions are offered on the basis of the data which have been presented. Although the study has been limited to only two carbonate aggregate types, these are felt to be representative of a large segment of potentially reactive carbonate rocks. For the conditions investigated in this study, which included measurement of properties to an age of one year, it is concluded that:

1. The expansion of concrete containing alkali-reactive carbonate aggregates is greatly influenced in a predictable manner by the following interrelated factors: (a) degree of rock reactivity, (b) amount of reactive component present, (c) alkali content of the cement, and (d) conditions of storage.
2. If the aggregate is of a high degree of reactivity, dilution of the reactive aggregate with a non-reactive one, reduction of cement alkalies, or both, may be necessary if cracking is to be eliminated and expansion reduced significantly.
3. With mildly reactive aggregates similar to 1-X, remedial measures do not appear needed at this time.
4. The generally accepted specification limit of 0.60 percent for low alkali cement does not appear to be low enough to reduce the reaction with the highly reactive carbonate aggregate to an acceptable level even with aggregate dilutions of 50 percent.
5. With aggregate 1-8, a dilution of 50 percent and a reduction of alkalies (Na_2O

equivalent) to 0.40 percent appear warranted. If reduction of alkalies to this limit is not possible, then correspondingly greater dilutions must be used.

6. Aggregate 1-8 passes present ASTM and AASHO acceptance tests for physical soundness, but exhibits borderline performance when tested for resistance to freezing and thawing in accordance with ASTM C291 in concrete containing low or medium-low alkali cements. It exhibits poor resistance to freezing and thawing when tested with high and medium-high alkali cements.

7. The general performance of concrete containing aggregate 1-8 depends greatly on its exposure. Cracking is more prevalent in concrete exposed to the combined effects of reaction, freezing-and-thawing, and shrinkage than in that exposed to moist conditions of the laboratory, even though in the latter case the expansion is significantly greater.

8. The criteria established that undesirable performance is indicated by: (a) expansions of moist-cured specimens of 0.03 percentage points greater than those of corresponding reference concrete; and (b) similar excess expansions of 0.02 percentage points for outdoor exposure, compare favorably with indications of field performance and observation in documented cases of alkali-carbonate reaction.

9. In the tests reported in this paper a reliable indication of the one-year performance outdoors can be obtained from the 90-day moist cured data except in borderline cases, where the expansions involved are very low.

10. Strength tests have not been as indicative of concrete performance as other methods, such as volume change and durability measurements.

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Appendix

TABLE 10

SUMMARY OF ABSOLUTE EXPANSION VALUES
(Values Expressed as Percent Based on Length at 24 Hours)

Cement	Dilution	Moist			Dry			Outdoor	
		90 Days	6 Months	1 Year	90 Days	6 Months	1 Year	6 Months	1 Year
(a) Aggregate 1-8									
H	0	0.060	0.084	0.120	-0.027	-0.030	-0.024	0.039	0.068
MH	0	0.036	0.069	0.108	-0.033	-0.036	-0.033	0.024	0.048
ML	0	0.024	0.039	0.069	-0.045	-0.054	-0.045	-0.002	0.028
L	0	0.009	0.023	0.039	-0.048	-0.051	-0.051	0.002	0.008
H	25	0.063	0.081	0.112	-0.026	-0.033	-0.031	0.029	0.061
MH	25	0.039	0.063	0.084	-0.042	-0.042	-0.045	0.026	0.045
ML	25	0.027	0.039	0.063	-0.036	-0.039	-0.042	-0.007	0.020
L	25	0.009	0.021	0.030	-0.054	-0.045	-0.051	0.012	0.003
H	50	0.041	0.066	0.086	-0.022	-0.027	-0.033	0.020	0.052
MH	50	0.027	0.050	0.072	-0.030	-0.030	-0.030	0.008	0.037
ML	50	0.018	0.039	0.046	-0.036	-0.042	-0.042	0.010	0.019
L	50	0.017	0.045	0.048	-0.033	-0.033	-0.036	-0.005	0.020
H	75	0.023	0.036	0.060	-0.036	-0.038	-0.038	0.015	0.028
MH	75	0.018	0.033	0.054	-0.036	-0.030	-0.033	0.012	0.028
ML	75	0.012	0.030	0.044	-0.036	-0.027	-0.030	0.016	0.018
L	75	0.007	0.027	0.033	-0.039	-0.036	-0.030	-0.006	0.006
H	0[1]	0.010	0.008	0.033	-0.024	-0.024	-0.027	0.003	0.013
MH	0[1]	0.012	0.021	0.036	-0.033	-0.033	-0.036	0.008	0.014
ML	0[1]	0.009	0.020	0.030	-0.042	-0.036	-0.036	0.007	0.016
L	0[1]	0.007	0.011	0.030	-0.030	-0.030	-0.033	0	0.009
(b) Aggregate 1-X									
H	0	0.021	0.030	0.054	-0.024	-0.027	-0.024	0.014	0.050
MH	0	0.015	0.027	0.045	-0.024	-0.027	-0.015	0	0.017
ML	0	0.010	0.022	0.033	-0.030	-0.030	-0.033	-0.004	0.020
L	0	0.007	0.011	0.030	-0.024	-0.030	-0.033	-0.011	0.014
H	25	0.012	0.021	0.036	-0.024	-0.027	-0.027	0.009	0.030
MH	25	0.018	0.021	0.042	-0.027	-0.030	-0.027	0.001	0.020
ML	25	0.015	0.027	0.033	-0.027	-0.030	-0.033	0	0.024
L	25	0.011	0.021	0.033	-0.033	-0.033	-0.030	-0.006	0.016
H	50	0.009	0.021	0.039	-0.027	-0.030	-0.027	0.015	0.033
MH	50	0.012	0.021	0.045	-0.033	-0.033	-0.024	0.007	0.017
ML	50	0.027	0.033	0.037	-0.027	-0.021	-0.018	0	0.019
L	50	0.009	0.027	0.033	-0.036	-0.036	-0.033	0.007	0.015
H	75	0.012	0.015	0.045	-0.032	-0.039	-0.027	0.002	0.021
MH	75	0.015	0.033	0.033	-0.030	-0.033	-0.033	0.003	0.012
ML	75	0.017	0.030	0.033	-0.021	-0.018	-0.027	0.010	0.015
L	75	0.007	0.024	0.031	-0.039	-0.033	-0.036	-0.002	0.011
H	0[1]	0.010	0.008	0.033	-0.024	-0.024	-0.027	0.003	0.013
MH	0[1]	0.012	0.021	0.036	-0.033	-0.033	-0.036	0.008	0.014
ML	0[1]	0.009	0.020	0.030	-0.042	-0.036	-0.036	0.007	0.016
L	0[1]	0.007	0.011	0.030	-0.030	-0.030	-0.033	0	0.009

[1] Reference granite.

Alkali-Carbonate Rock Reactions in Michigan

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The Michigan State Highway Department has not so far experienced distress of field concrete positively identified as being due to cement alkali-carbonate rock reaction. However, laboratory studies have found three quarried limestones having very mild expansions when incorporated in concrete made with alkali cement. Nineteen other limestones and seventeen natural gravels similarly studied show negligible expansions. Expansion data up to 4 years age are presented for several of the aggregates studied. Two of the limestones which are mildly reactive exhibit dependence of freeze-thaw durability on the alkali content of the cement when the aggregates are placed in the concrete in a vacuum saturated condition. Durability is improved with low alkali cement. The third mildly reactive limestone has not been similarly studied because its freeze-thaw durability even with high alkali cement is good, and it is doubtful that improvement in durability with low alkali cement, if present, could be reliably measured. Deficiencies in the completeness of the present data exist because only portions were produced on a planned research basis. The remainder was obtained as a minor supplement to routine acceptance testing.

•IN 1957 Swenson (1) reported laboratory work on Kingston, Ont. limestone following observation of abnormal expansion in field concrete containing this carbonate rock as coarse aggregate. Expansions were found to be related to alkali content of the cement and were most successfully predicted by observation of expansion bars stored in the ordinary laboratory moist curing room. The simplicity of Swenson's procedure was attractive and led the Michigan State Highway Department Testing Laboratory to make expansion bars on a routine basis simultaneously with concrete batches for freeze-thaw evaluations of aggregates. It seemed possible that potential destructiveness of aggregates, heretofore unidentified as to cause, may have been overlooked and additional data could be acquired rather easily. However, destructive reactions in field concrete have not yet been confirmed in Michigan due either to alkali-aggregate reaction or to alkali-carbonate rock reaction.

Three carbonate rock sources in Michigan give mild expansions with moderately high alkali cement in laboratory moist room storage, but field observations of structures containing these aggregates have not shown adverse effects. Other limestone (as used here, the term limestone refers to rock composed basically of calcite and/or dolomite) sources available to the Michigan market have not shown appreciable expansions in laboratory observation nor have any of the glacial gravels investigated. Of greater perplexity is the observation that two limestones having mild expansion in moist room storage demonstrate considerable sensitivity to cement alkalies in freeze-

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thaw durability tests. Much better durability is developed with low alkali cement. This behavior is similar to that reported by Tremper (2) for certain aggregates in the State of Washington.

TEST PROCEDURES

Expansion bars, 2 by 2 by 11 in. fitted with stainless steel measuring studs, have been made simultaneously with casting concrete prisms for freeze-thaw durability determinations. The procedure used by the laboratory is to make one expansion bar and three 3- by 4- by 16-in. freeze-thaw prisms from each of three batches of concrete made on three different days for each cement-aggregate combination. Thus, three expansion bars and nine freeze-thaw prisms are provided for each evaluation.

The coarse aggregate under test is split into four sieve sizes, $\frac{3}{4}$ to 1 in., $\frac{1}{2}$ to $\frac{3}{4}$ in., $\frac{3}{8}$ to $\frac{1}{2}$ in., and No. 4 to $\frac{3}{8}$ in., recombined into equal amounts of each size and then vacuum saturated and soaked 24 hours prior to incorporating in concrete. The fine aggregate used in all tests was from a single local natural aggregate source, and was regraded to provide the following gradation (percent passing): No. 4 sieve, 100; No. 16 sieve, 70; No. 50 sieve, 17; No. 100 sieve, 2. The concrete is proportioned to contain 5.5 sacks of cement per cubic yard with a 2- to 3-inch slump. The concrete is air entrained using Type I cement with sufficient neutralized vinsol resin solution added to maintain the air at 5 to 6 percent. Freeze-thaw beams are cured under water for 14 days at which time they enter the freezing chamber, using ASTM Method C291, "Resistance of Concrete Specimens to Rapid Freezing in Air and Thawing in Water." Eight cycles of freezing and thawing are obtained per day. Durability factor is computed, based on 300 cycles and a reduction in sonic modulus of 30 percent. Expansion bars are stored in the 73 F moist room immediately after casting, and the molds are removed the following day at which time initial length measurements are taken. Expansion bars remain in the fog curing room and length changes are observed at monthly intervals using a comparator with a 0.0001-in. dial. Corrections of the comparator are made using an invar reference bar.

Strength specimens for 7 and 28 days both in flexure and compression are made from each batch as well as calculation of w/c ratio, weight per cubic foot, etc. To conserve space, the latter data will not be presented unless special interest should develop and make it desirable to do so.

TEST RESULTS

Since the beginning of making expansion bars simultaneously with conducting freeze-thaw evaluations, 17 gravel samples have been studied ranging from very poor to excellent durability. The gravels have been produced using a variety of processing at different sources, ranging from simple washing and screening to heavy media separation, elastic fractionation, or jigs. Most of these glacial gravels originated in the southern peninsula of Michigan but one came from northern Illinois. Figure 1 is a composite of the observed moist room expansions giving an envelope within which all values have fallen. All 51 specimens are at least one year old and some are as old as 5 years. From present trends, it is highly unlikely that any specimens will fall outside the dashed lines shown for the older ages. These bars were made in all cases using cements with alkali contents, expressed as Na_2O equivalent, between 0.67 and 0.85 percent. In nearly all cases, the cement consisted of a blend in equal amounts of three brands. As expected, the observed expansions are small and exhibit no tendencies typical of the alkali-carbonate reaction.

Figure 2 shows similar data for 19 limestone samples. The quarries from which these originated, range from northern Ohio and Illinois to northern Michigan. Extrapolation of the data out to 4 years age was made similarly to that of the gravels and appears entirely justified by the data presently available. In this case, all specimens were made with cements having alkali contents ranging from 0.67 to 0.82 percent. These particular limestones exhibit expansions only slightly greater than that of the gravels. This behavior contrasts with that of three other limestones, data on which are shown later.

was stabilized in tap water and each cylinder was then immersed in NaOH solution in a separate polyethylene container.

Length measurements were made weekly using a dial comparator calibrated to 0.0001 in. At the end of 1 yr, tests on many specimens showing no expansion were discontinued and length measurements on the remaining samples were made at longer intervals. The expansive samples are still under test.

Water absorption determinations were made on all specimens, but the data are too numerous to be included in this paper.

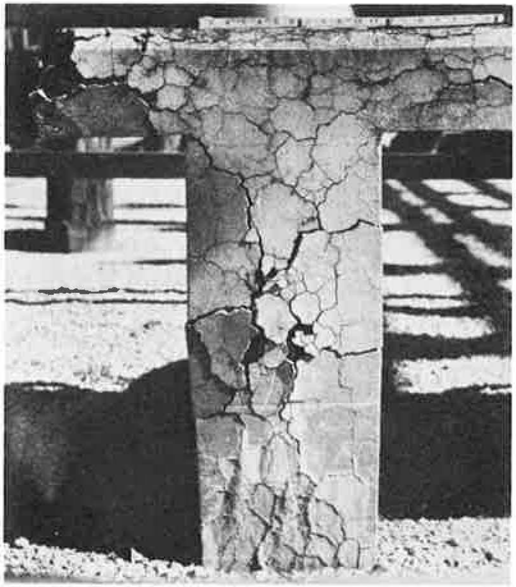

Figure 1. Deteriorated concrete with Gull River carbonate rock as coarse aggregate.

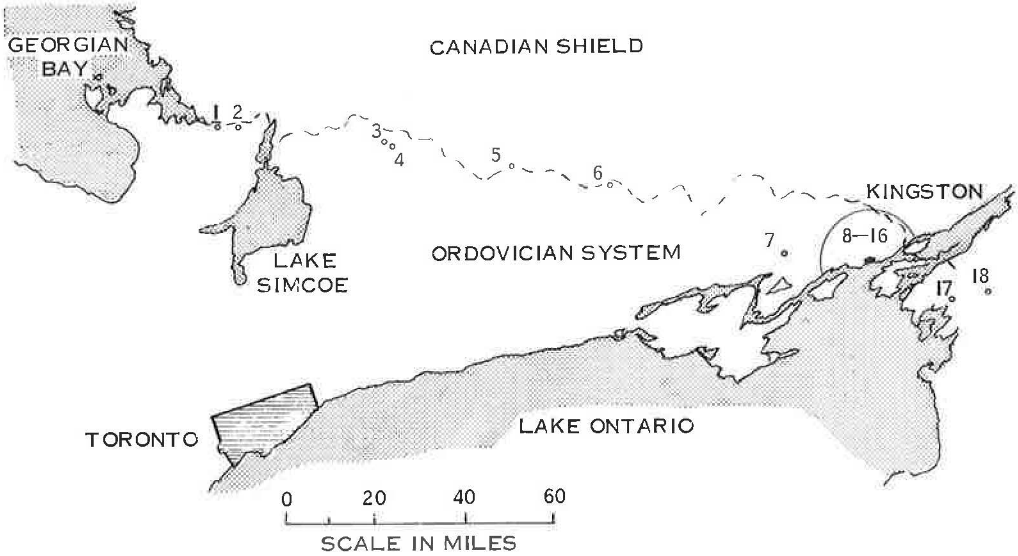

Figure 2. Locations of sampled Gull River rocks.

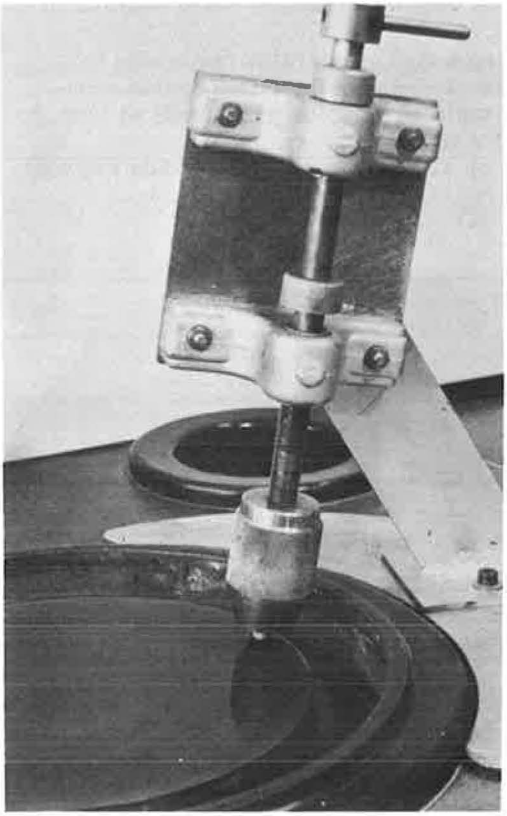

Figure 3. Jig and grinding lap for cutting cylinders conically to required length.

Petrographic Examinations

Because several petrographic features are reported to be significant for carbonate rocks showing expansion in concrete, material adjacent to the locations in the samples from which the test cylinders were taken was examined. All specimens were examined in thin sections for determination of texture and general composition. The percentage of noncarbonate impurities was determined using a 20 percent HCl solution at a maximum temperature of 60 C. Cursory determination of the type of carbonate rock (limestone or dolomite) was made by means of the copper nitrate staining test (2).

On the expanding samples only, partial chemical analysis was carried out to establish the calcite to dolomite ratio, and quantitative X-ray analysis of the acid insoluble material was conducted by R. Laakso of the Ontario Department of Mines to establish the type and approximate amount of noncarbonate impurities; i.e., the clay minerals and the main clastic minerals. X-ray diffractometry was also used to confirm the calcite to dolomite ratio calculated from chemical analyses.

RESULTS OF EXPANSION TESTS

Up to this time, a total of 170 cylinders (including four cylinders that showed definite expansion but broke after 4 to 29 wk of immersion) representing 17 Gull River locations have been immersed in 1 N NaOH solution for periods of from 1 to 2 yr. After immersion in NaOH most of the cylinders showed changes in size and some showed cracking.

Sixty-one cylinders representing eight locations expanded more than 0.1 percent, considered to be the lower limit of significant expansion. Of the comparison samples only five cylinders from the gravel particles were of the expansive type and are included in the following discussion on expanding Gull River carbonate rocks.

Cracking of the cylinders immersed in NaOH indicated the presence of spots or zones of weakness in the rock which would not necessarily cause cracking in concrete[1] where the rock is confined. The fact that highly cracked specimens (Fig. 13, Appendix) may not break indicates that the zones promoting cracking are normally very limited.

Amount of Expansion vs Duration of Exposure to NaOH

The 66 expanding cylinders may be divided into three groups based on the amount and time of maximum expansion observed:

1. Minor-expansion group[1]—expansion from 0.10 to 0.39 percent.
2. Early-major-expansion group—expansion of at least 0.40 percent, showing expansion in 2 to 5 wk. This group usually reached its maximum expansion in 10 to 40

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[1] The lower limit allows an appropriate margin for testing error; the upper limit was selected arbitrarily.

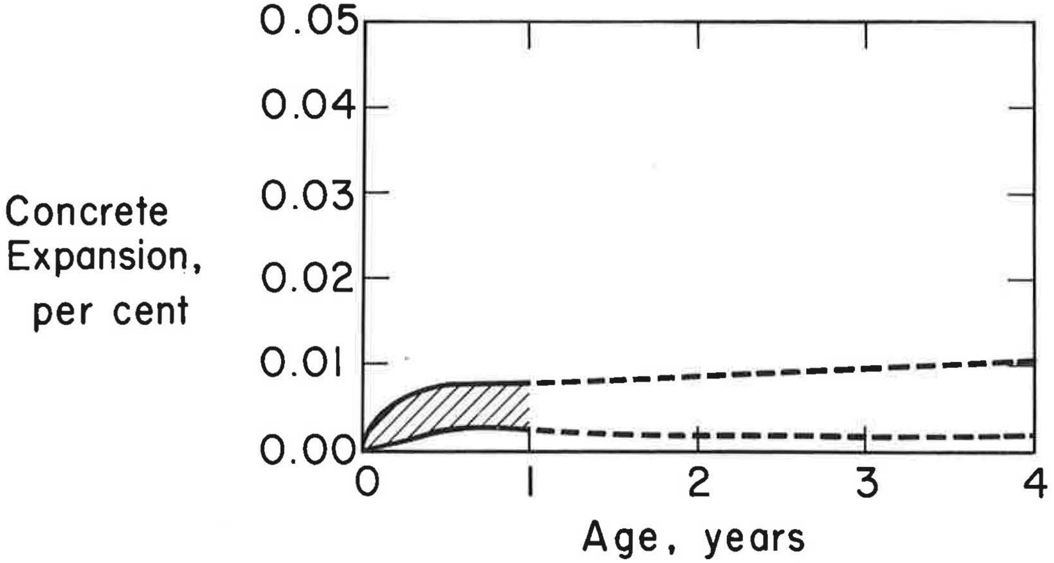

Figure 1. Envelope of expansions of moist stored concrete made with 17 different glacial gravels.

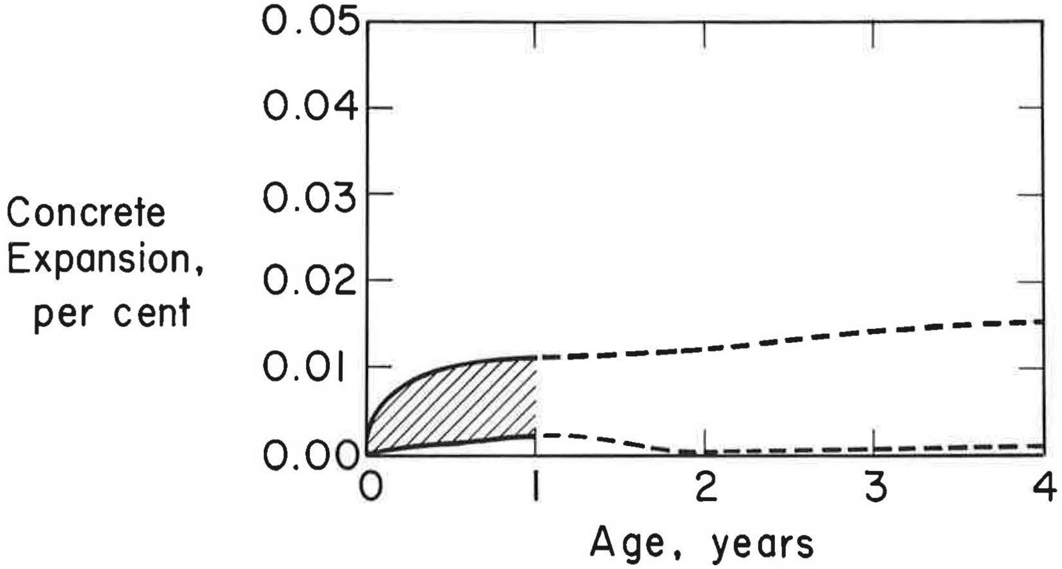

Figure 2. Envelope of expansions of moist stored concrete made with 19 different non-reactive limestone coarse aggregates.

TABLE 1

CONCRETE EXPANSIONS AND FREEZE-THAW DURABILITY RELATED TO CEMENT ALKALIES FOR LIMESTONES NO. 1 AND NO. 2

Series	Coarse Aggregate	Cement		Freeze-Thaw Durability Factor	Moist Storage Concrete Expansion, 4 yr (%)
		Designation	Alkali, Na_2O Equiv. (%)		
No. 1	Limestone no. 1	A	0.80±	32	0.036
	Gravel no. 1	A	0.80±	38	0.005
	Gravel no. 2	A	0.80±	8	0.007
No. 2	Limestone no. 1	B	0.21	63	0.013
	Limestone no. 1	C	0.68	20	0.031
	Limestone no. 1	D	0.85	29	0.043
No. 3	Limestone no. 1	E	0.26	80	0.010
	Limestone no. 2	E	0.26	80	0.007
	Gravel no. 5	E	0.26	13	0.004
	Limestone no. 1	F	0.60	41	0.023
	Limestone no. 2	F	0.60	65	0.012
	Gravel no. 5	F	0.60	13	0.009
	Limestone no. 1	G	0.87	19	0.038
	Limestone no. 2	G	0.87	32	0.017
	Gravel no. 5	G	0.87	12	0.008

Routine freeze-thaw testing of one limestone (identified as No. 1, hereafter) several years ago revealed two items: (a) the durability factor was considerably lower than expected, and (b) this was accompanied by appreciably greater expansions of the accompanying moist stored expansion bars. Two companion gravel samples tested simultaneously had the usual low expansions and poor to mediocre durability as would be predicted from the known content of deleterious particles. Unfortunately, the exact alkali content of the particular lot of cement from which these specimens were fabricated is unknown. However, this testing was performed with cement from a single source, and prior and subsequent tests of cement from this mill indicated the probability of about 0.8 percent alkali. These tests are identified as Series No. 1 in Table 1.

To verify that this limestone was sensitive to alkali content of the cement, Series No. 2 tests (Table 1) were conducted wherein three cements of determined alkali content were individually incorporated with limestone No. 1 in freeze-thaw specimens and expansion bars. These tests revealed a definite pattern of greater expansion with the high alkali cement accompanied by interior laboratory freeze-thaw durability. The durability factor of 20 with the intermediate alkali cement versus 29 with the highest alkali cement is not in strict order of decreasing durability with higher alkali cement. However, the substantially improved durability with the lowest alkali cement is unmistakable. At the time, it was not realized that the major expansion would take place within about the first 24 months for this limestone, and it seemed possible that very substantial expansions would ultimately occur. This has not proved to be the case.

To confirm better the pattern of behavior which was observed, a third series of tests was devised wherein cements of three alkali contents were individually incorporated in concrete containing each of three aggregates, one of which was limestone No. 1 which had shown tendencies for expansion in moist curing room storage. The second material selected for this series was a crushed limestone (No. 2) from a quarry which has been considered of borderline acceptability for many years. This stone typically breaks into slabby particles when crushed and requires fairly high sand contents in concrete to maintain workability with consequent high water demand. Sulfate soundness losses are typically high. Examination of pavements using limestone No. 2 as a coarse aggregate reveals rather frequent shale pop-outs but has not positively established poor service behavior, and the stone is widely used in its market area. The Department does not permit its use in exposed concrete in structures. The third aggregate selected for this series was a natural gravel (No. 5) which has been widely used without serious doubts as to its intrinsic durability but which has a chert and soft stone content contributing to numerous pop-outs. Heavy media treatment of this gravel has subsequently been successful in alleviating this problem.

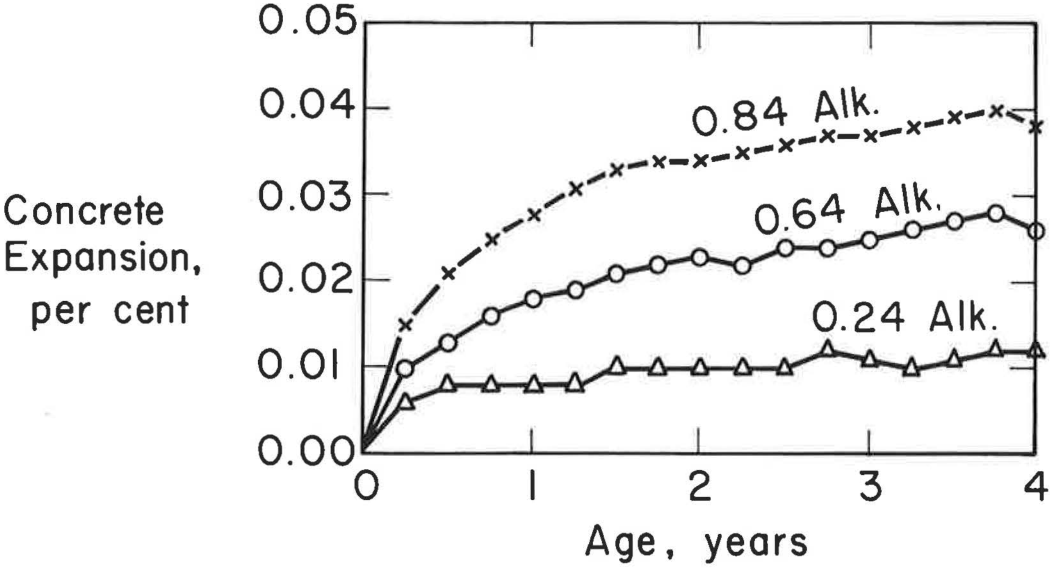

Figure 3. Effect of cement alkalies on expansion of concrete made with mildly reactive limestone no. 1.

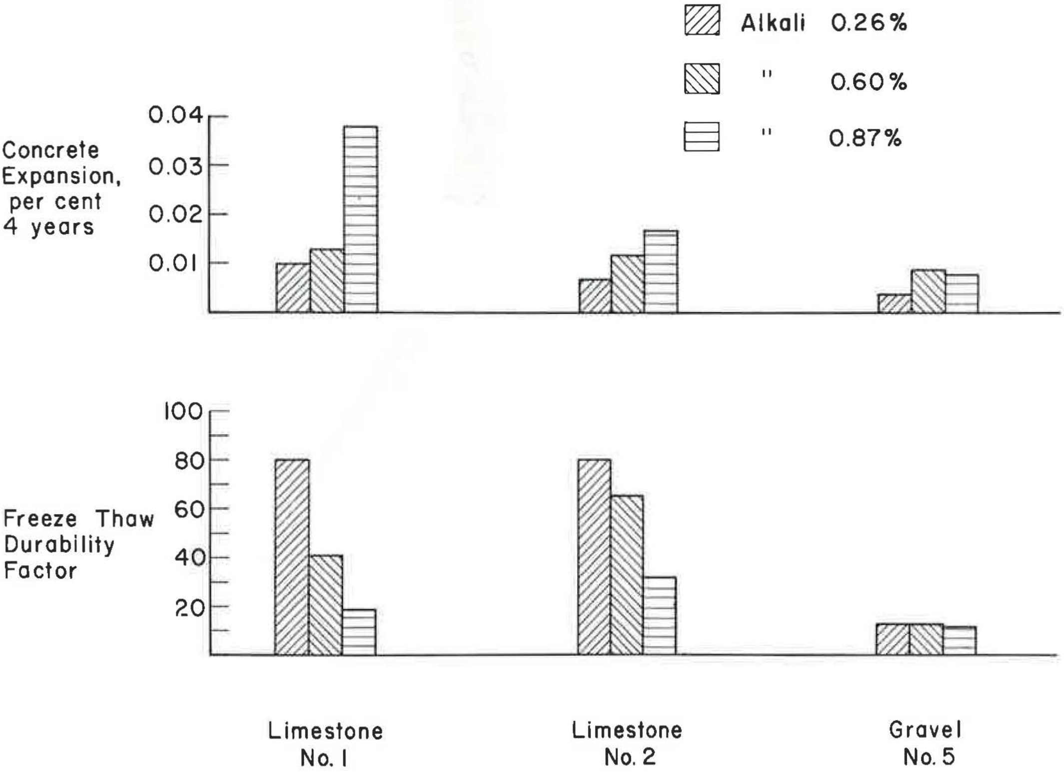

Figure 4. Series No. 3 tests of three coarse aggregates in concrete containing cements of three alkali contents.

TABLE 2

CHEMICAL ANALYSES OF CEMENTS USED IN SERIES 1, 2 AND 3 TESTS

Determination	Analysis (%)						
	A[1]	B	C	D	E	F	G
Silicon dioxide, SiO_2	20.4	20.5	20.9	20.7	21.0	21.2	21.3
Aluminum oxide, Al_2O_3	6.1	5.8	4.9	5.8	5.7	5.1	5.3
Ferric oxide, Fe_2O_3	2.8	2.2	2.9	3.1	2.4	2.6	2.7
Calcium oxide, CaO	64.3	62.5	63.0	62.3	63.0	63.4	64.1
Magnesium oxide, MgO	2.4	3.4	3.3	3.8	2.9	3.3	2.4
Sulfur trioxide, SO_3	2.5	2.3	2.3	1.9	2.3	2.4	2.1
Loss on ignition	1.2	2.7	1.5	1.2	1.8	1.3	0.9
Sodium oxide, Na_2O	0.21	0.14	0.21	0.27	0.15	0.20	0.40
Potassium oxide, K_2O	0.90	0.11	0.72	0.88	0.16	0.61	0.72
Insoluble residue	0.24	0.31	0.09	0.14	0.11	0.12	0.10
Total alkali, Na_2O equiv.	0.80	0.21	0.68	0.85	0.26	0.60	0.87
Calculated compounds:							
C_3S	55	50	54	47	49	52	54
C_2S	17	21	19	24	24	22	21
C_3A	11	12	8	10	11	9	9
C_4AF	9	7	9	9	7	8	8

[1] Chemical analysis of cement from mill at about the time Series No. 1 specimens were made (Table 1).

TABLE 3

CHARACTERISTICS OF LIMESTONES

Limestone No.	Sp. Gr. Bulk Dry	Absorption (%)	Dolomite/Total Carbonate Ratio	Insoluble Residue (%)
1	2.65 - 2.67	0.94 - 1.13	0.26	10.6
2	2.62	1.22	0.05	21.4
3	2.71	1.04	0.57	7.7
4	2.65	0.63	0.06	1.2
5	2.63	2.06	0.96	4.5
6	2.72	1.30	0.95	4.9
7	2.60	2.37	0.96	—
8	2.62	1.83	—	—
9	2.63	1.92	—	—
10	2.45	2.67	—	—
11	2.53	2.37	—	—
12	2.76	0.53	0.98	0.7
13	2.62	1.64	0.97	0.5
14	2.58	1.15	—	—
15	2.31	4.63	—	0.7
16	2.59	1.31	—	0.4
17	2.60	1.07	—	2.9
18	2.63	0.89	—	3.4
19	2.57	1.92	—	2.0
20	2.54	2.51	—	2.7
21	2.64	0.84	—	3.8
22	2.62	1.84	0.95	—

In conducting the Series No. 3 tests every effort was made to provide strictly comparable specimens by rotating the making of the nine combinations of materials (27 batches). All specimens were placed side-by-side in the moist room and scheduled into freeze-thaw in strict rotation to compensate for time-dependent variations. Because there were 81 beams involved that exceeded the capacity of the freeze-thaw equipment, making of test batches was delayed until there was assurance that the beams could be accommodated in the freeze-thaw chamber.

Expansion curves for concrete containing limestone No. 1 and using cement with three levels of alkali content are shown in Figure 3, up to an age of four years. The curve for the higher alkali cement is an average of values obtained in Series 1, 2 and 3. The curves for moderate and low alkali cements are averages of results from Series 2 and 3.

The results of the No. 3 series of tests are given in Table 1 and shown in Figure 4. Limestone No. 1 again shows larger concrete expansions accompanying its use with higher alkali cement as was indicated in the Series No. 2 tests. Conversely, the freeze-thaw durability factor diminishes with increased cement alkalies. Limestone No. 2 shows similar responses to cement alkalies but to a lesser degree. The gravel appears to be entirely insensitive to cement alkalies both as to expansion and freeze-thaw durability. Chemical analyses of the cements used in these tests are given in Table 2.

Limestone No. 3 from another quarry in the same general geological formation as limestone No. 1 was tested later and has shown 0.02 percent expansion at 2 years. This limestone was tested with a moderately high alkali cement, 0.82 percent, but had a relatively high durability factor of 86.

Evidence is not conclusive that other limestones, not showing expansion in moist room storage, would likewise display durability related to alkali content of the cement. However, several of the limestones incorporated with moderately high alkali cement and whose low expansions are reported in Figure 2 had high durability factors (in the 80's or 90's), and it seems unlikely that use of low alkali cement would show much improvement in durability.

The second line of evidence showing that the unusual freeze-thaw behavior of these limestones may be related to their expansions in moist room storage is somewhat more tenuous. This relates to their chemical composition which confirms, to a degree, the observations of Hadley (3). Table 3 lists the dolomite-total carbonate ratio and insoluble residue determinations, where available, for the limestones reported in this study. Dolomite was determined by wet chemical analysis on the assumption that all the magnesium carbonate occurred as dolomite (54 percent calcium carbonate and 46 percent magnesium carbonate) and the remainder of the calcium carbonate as calcite. Insoluble residue was determined using 3N hydrochloric acid as suggested by Lemish et al. (4). Limestones Nos. 1 and 3 have shown concrete expansions in moist storage and approach the intermediate dolomite content, with simultaneous appreciable insoluble content, which Hadley found to be significant criteria for distinguishing alkali-sensitive limestones. Limestone No. 2, although having a low dolomite content, has a high insoluble content which may explain its expansion behavior.

SUMMARY

1. Michigan's experience to date with alkali-carbonate rock is largely negative. Only three limestones have been found displaying expansive characteristics when incorporated in concrete with high alkali cement and subjected to moist room storage, and none of these expansions is of such magnitude, even after 4 years, as to predict adverse field behavior. Stone from one of these quarries has been used for more than 40 years as concrete coarse aggregate but is acknowledged to be the subject of controversy as to satisfactory service record. The present study would predict better performance if used with low alkali cement. None of the gravels studied shows significant expansions under similar exposure.

2. Two of the three limestones showing mild moist room expansions display much improved freeze-thaw resistance, when vacuum saturated in concrete, if used with a low alkali cement. The third limestone (No. 3) has not yet been studied in this regard but in view of its good durability with a high alkali cement, no appreciable improvement would be expected. The authors postulate that for limestone No. 1, dedolomitization in the freeze-thaw beams during the 14-day submerged curing period opens up the internal rock structure allowing greater water penetration and thus greater vulnerability to frost attack. In the case of limestone No. 2, inasmuch as the dolomite content is so low, it seems more likely that the large insoluble content is playing the dominant role.

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Variations in Performance of Concrete with Carbonate Aggregates in Iowa

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Observation of concrete pavements over a period several years indicates that the majority of the carbonate aggregates used can be expected to perform satisfactorily for at least 20 to 25 years. Several aggregates from various geologic sources were used in concrete pavement that is more than 40 years old. Of more than 75 carbonate aggregate sources used, only a few have been associated with early deterioration of concrete.

Concrete deterioration associated with one geologic source of the coarse aggregate was recognized in Iowa in the early 1930's in pavement less than 10 years old. Since then, observations indicate that in some other cases of deterioration there appears to be a relation between the concrete durability and the geologic source of the coarse aggregate. Of the cases recognized, deterioration is first noticed in pavements ranging in age from 3 to 23 years. In these cases, deterioration progresses rapidly and is generally severe within five years after it is first observed.

The aggregates associated with deterioration are from rock formations ranging in age from Ordovician to Pennsylvanian. Rock types have a wide range of physical, chemical, and engineering properties similar to aggregates that have satisfactory performance. Of the aggregates associated with deterioration, current specifications and test limits have eliminated the carbonate rocks that have a high insoluble residue content, other than quartz sand and chert. There are still three known geologic sources capable of meeting current test limits. They are associated with concrete that has shown extensive deterioration on pavements ranging from 8 to 15 years old. These three are in different stratigraphic horizons with different lithologies, but have no distinctive properties that separate them from acceptable geologic sources. They are 95 percent or better total carbonate.

One of the basic research programs of the Iowa State Highway Commission for more than 20 years has been a study of the behavior of concrete made with aggregates from different sources. The program includes a study of the physical, chemical, and geologic properties of various coarse aggregates and of the properties of the concrete containing these aggregates. The purpose of this study is to relate these characteristics to the behavior of the concrete in service, and thus develop better methods for determining the probable performance of proposed materials.

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Several selected case histories are reported to illustrate the various aspects of the problem and the methods used to relate the characteristics of coarse aggregate to concrete durability.

•A STUDY is being conducted by the Iowa State Highway Commission of the physical, chemical, and mineral properties of various coarse aggregates and of the properties of concrete containing these aggregates. It is the purpose of this study to relate these properties to the behavior of concrete in service and to develop better methods for determining the probable performance of proposed materials. The aggregate studies are a part of a continuous program of study on the performance of concrete that has been conducted for more than 30 years.

Continued observations of concrete indicate that the majority of the portland cement concrete pavements more than 30 years of age, containing carbonate aggregate, attain this age without any signs of serious deterioration. Some pavements are more than 40 years old and the concrete is still in excellent condition. Some other pavements have shown signs of deterioration (as defined in this paper) at ages ranging from 3 to 23 years. Deterioration that has become severe in pavements under 25 years of age has been associated with aggregate produced from ten different geologic sources. A geologic source of aggregate is defined as a particular stratigraphic horizon with known properties within a defined geographic area.

Study on five of these sources has shown that it is possible to establish a range in age at which the concrete containing aggregates from these sources will begin to show deterioration. These age ranges which generally span about five years seem to be consistent for a wide range of variables described herein.

It is recognized that the performance of concrete pavements with any one coarse aggregate may be affected by traffic as related to structural adequacy, site conditions and design features which change the amount of stress a pavement experiences. Although the variations in performances due to these factors are recognized, it is considered that within the broad general classifications of pavement performance defined in this report, the effects are within a range that allows a relationship between the geologic source of the coarse aggregate and pavement performance to be developed.

Deterioration was first associated with the geologic source of the coarse aggregate in the early 1930's. In this case the pavements were less than 5 years of age. Since that time extensive research has been conducted to develop tests on aggregate and concrete that will correlate with the performance of concrete pavements. Current specifications include tests developed under this program which eliminate seven of the recognized unsatisfactory aggregates. So far no diagnostic characteristics have been found to identify the remaining three aggregates with unsatisfactory service.

This paper presents a summary of the data that defines the current status of the carbonate aggregate problem in Iowa. It is only a partial summary of ten typical geologic sources representing more than 75 known carbonate aggregate sources and does not include any of the data available on more than 100 gravel sources that have been used.

The purpose of this presentation is (a) to show the accumulated evidence that associates the geologic source of the coarse aggregate with variations in concrete performance, and to show examples of concrete deterioration at successively greater ages; and (b) to describe the rock and concrete properties associated with satisfactory and unsatisfactory service.

RECORDS

Centralized records have been maintained on all portland cement concrete paving projects constructed under supervision of the Highway Commission. Records for all projects are available on construction data and sources of materials used. There are also records of crack or condition surveys that have been made for many projects.

Records are maintained for each source of material used in construction. All records, from initial prospecting to the present, are kept at one location in the files. For quarries, all test records are generally related to a geologic section for the quarry.

These records on aggregate and construction form a basis for establishing an informal classification for pavement service and categories for concrete aggregate service life.

During the past several years inspections have been made on pavement projects ranging from two to more than 40 years of age. Several selected sections of pavement for each of various geologic sources have been inspected at least once each year during the past five years. Current inspection reports generally include a description of the pavement surface and joint and crack condition. Patch counts are made and photographs are taken of the typical conditions of each section surveyed.

When deterioration is noted, other pavements containing aggregates from the same geologic source are examined and photographed. Inspections are conducted frequently on concrete showing signs of deterioration to determine the rate of deterioration. For each new geologic source one or two representative sections of pavement are selected to be checked at random intervals for pavement condition.

GUIDE FOR PAVEMENT CONDITION CLASSIFICATION

The current pavement condition classification is based on the comparative condition of all pavements inspected. Most of these have been in service for 35 years with some as long as 40 years or more. This classification is an attempt to develop a systematic method of categorizing concrete performance. Table 1 was developed from concrete condition survey reports.

CURRENT SPECIFICATIONS

Current specifications for concrete aggregate are contained in the Iowa Standard Specifications, Series of 1960. The physical test limits are as follows: Abrasion loss determined in accordance with AASHO T-96, grading A or B shall not exceed 50 for crushed stone that is consistently 90 percent or more calcium carbonate, and 45 for all other crushed stone. The percentage loss on 16 cycles freezing and thawing in water alcohol solution, method "A", shall not be greater than 6. 0.

COARSE AGGREGATE CLASSIFICATION

More than 75 sources of rock have been used for coarse aggregate in concrete in Iowa. Most of these have been tested by current methods. On the basis of performance records and test results more than one-half of the aggregate sources can be placed in one or another of the four major categories in Table 2.

To date, ten geologic sources have been associated with deterioration. All but three are eliminated by current test limits and of these three only the Otis is still being used. This source is under study at this time.

To illustrate the problem and variations in service life, the case histories of ten typical geologic sources are described. Each case history includes a description of the geology of the source and the service record associated with the aggregate from each source. Five case histories are for satisfactory and five are for unsatisfactory aggregates. Data on construction and condition surveys for typical sections of pavement are given in Table 3. Chemical analyses and rock properties for each source are given in Tables 4 and 5.

SATISFACTORY SERVICE

Satisfactory service of more than 30 years is known for concrete containing carbonate aggregates from 15 geologic sources in several stratigraphic horizons with various lithologies. Five of these geologic sources have been used for concrete that shows no signs of deterioration after 40 years of service.

Figure 1 shows the general condition of pavements ranging from 33 to 42 years old containing satisfactory aggregates. For pavements constructed before 1929 with no transverse joints, the transverse crack spacing varies from about 20 ft to more than 100 ft. The concrete is in excellent condition with no evidence of progressive deteri-

TABLE 1

DESCRIPTION OF PERFORMANCE FOR SATISFACTORY AND UNSATISFACTORY SERVICE

Classification	Age (yr)	Performance Description[1]
Satisfactory[2]	0-10	Absolutely no failures or signs of potential failure due to aggregate should be expected, except occasional pop-outs, spalls, development of expected transverse cracks and some diagonal corner cracks[1].
	10-20	Concrete should have essentially no progressive failure due to aggregate. Toward the 20-yr age there may be some "D" line cracking[1] showing around cracks and construction joints or there may be some discoloration that may be associated with future development of "D" line cracks. However, concrete should not show progressive scaling[1]. Many pavements have reached this age with as few as two or three patches per mile and no "D" line cracking.
	20 30	Sometime after 20 years some pavement patching would be anticipated. Amount of patching would be small at first and increase slightly each year. Cracks and joints are expected to begin to show progressive scaling toward 30 years of age.
Unsatisfactory	0-20	Concrete begins to show development of discoloration associated with "D" line cracks or map cracking[1], curb disintegration, severe spalling, and progressive scaling that results in pieces of concrete becoming dislodged under traffic on more than 5 percent of the joints and cracks and requires continuous and extensive patching. The number of full-width patches per mile increases rapidly with time. In severe cases, entire slab shows cracking and spalling. These various conditions are shown in Figures 2, 3, 5, 6, 7. There conditions may begin to occur at any age up to 20 years. In some pavements deterioration has begun occurring at 25 years of age and becomes severe at 30 years or more of age. Cracking and disintegration of concrete generally continues in old concrete adjacent to patches.

[1] Terms as defined in Appendix B., HRB Special Report 30, Pavement Condition Surveys (1957).

[2] Majority of pavements have far exceeded the satisfactory criteria; at age of 40 years some pavements show no deterioration.

TABLE 2

COARSE AGGREGATE CLASSIFICATION ACCORDING TO TEST RESULTS AND PERFORMANCE IN CONCRETE[1]

Performance	Class.	Description
Satisfactory	I.	Aggregates complying with current test limits, no signs of deterioration in concrete after: (a) 20 years of service, 20 sources; (b) 30 years of service, 10 sources (Dubuque Stone)[1]; and (c) 40 years of service, 5 sources (Alden, Davenport, Iowa City)[1].
	II.	Aggregates not complying with test limits: 30 years of service, 2 sources (Farmington)[1].
Unsatisfactory	III.	Aggregates complying or nearly complying with current test limits: deterioration begins on concrete less than 20 years of age, 3 sources (LeGrand, Decorah, Otis)[1].
	IV.	Aggregates that do not comply with specifications; deterioration begins in concrete at: (a) less than 20 years of age, 9 sources (Glory)[1]; and (b) less than 25 years of age (Fayette)[1].

[1] Some aggregates with less than 10 years service or where concrete condition is not known are not classified. Number of sources listed is for carbonate aggregates only. Sources used as examples are listed by name.

TABLE 3

PAVEMENT CONSTRUCTION AND CONDITION DATA, 1963[1]

Project		Year Built	Thickness (in.)		Joint Spacing		Cement	Sand	Coarse Aggregate	Miles	"D"Cr.	Prog.[4] Scale	Avg. No. Patches per Mile[5]		Age (yr)	Concrete Condition
Co.[2]	Cd.[3]		Edge	Uniform	Exp.	Contr.							1958	1963		
(a) Satisfactory Performance																
42	22	1931	10	7	80'	None	2	2	Alden	9	No	No	—	1-3	32	Very good
85	5	1929	10	8	40'4"	None	1	1	Alden	6	No	No	—	2-10	34	Good
31	13	1932	10	7	60'	None	4	4	Dubuque	17	No	No	—	—	31	Very good
3	4	1931	10	7	80'	None	4	3	Dubuque	5	No	No	0	0-3	32	Excellent
28	1	1928	10	7	None	None	3	4	Dubuque	10	Yes	Some	2-3	5-10	35	Good, signs of deterioration
52	7	1927	10	7	None	None	5	6	Iowa City	12	No	No	0-1	0-3	36	Excellent for Coralville Ls.
52	2	1921	7	8	None	None	4	5	Iowa City	2	No	No	0-5	0-5	42	Very good to excellent
89	4	1930	10	7	None	None	5	8, 9	Davenport	5	No	No	0-1	0-2	33	Very good
89	1	1928	10	7	None	None	5	7	Davenport	7	No	No	0-2	0-2	35	Excellent
52	5	1927	10	7	None	None	1	6	Davenport	5	No	No	0-5	0-5	36	Very good, occasional blow-up
82	15	1923	8	8	None	None	9, 10	5	Davenport	3	No	No	—	1	40	Excellent
89	4	1930	10	7	None	None	5	8, 9	Farmington	5	No	No	0-1	0-2	33	Very good
(b) Unsatisfactory Performance																
86	6	1930	10	7	None	None	8	18	Glory	4	Yes	Yes	—	75-100	33	200 + patches in 2 miles
Typical of many projects, sands, cements and designs									Glory[6]	100+	Yes	Yes	—	100-300	—	Very poor at 15 + years
28	15	1942	10	7½	120'	30'	5	10	Fayette[7]	8	Yes	Yes	0	0-1	21	3 patches in 8 miles
28	14	1940	9	6	120'	30'	1, 6	11	Fayette	15	Yes	Yes	0	7-20	23	70-90% of joints affected
28	11	1939	9	6	202'8"	25'4"	4	19	Fayette	3	Yes	Yes	0	15-30	24	Fair to poor at all joints & cracks
28	10	1936	10	7	60'	30'	3	12	Fayette	4	Yes	Yes	—	20-50	27	All joints & cracks deteriorating
85	11	1938	10	7½	90'	30'	2	13	LeGrand	6	Yes	Yes	—	70-90	25	Fair to poor, 535 patches
86	2	1927	10	7	None	None	3	14	LeGrand	1	Yes	Yes	—	35	36	95% of all joints & cracks affected
Typical of many projects, sands, cements and designs									LeGrand	100+	Yes	Yes	—	50-100	—	Very poor at 15 + years of age
96	18	1932	10	7	80'	None	5, 4	15	Decorah	7	Yes	Yes	75-100	100-175	31	Very poor, over 700 patches
Typical of many projects, sands, cements and designs									Decorah	45	Yes	Yes	10-30	25-100	—	Occasional good sections
57	54	1952	10	8½	None	20'	5	17	Otis	6	No	No	0	0	11	Very good, occasional spall
28	17	1948	8	7	As on	Plans	7	3	Otis	8	Yes	No	—	0-4	15	Good, 33 patches in 8 miles
64	22	1947	10	9	None	None	2, 4	16	Otis	6	Yes	Yes	Occas.	5-35	16	Fair
57	38	1946	10	8	120'	30'	5	17	Otis	5	Yes	Yes	Occas.	5-30	18	Fair
52	26	1941	10	7½	120'	30'	2	17	Otis	4	Yes	Yes	3-10	15-40	22	10-15% of all joints, as in Fig. 7b, right
52	23	1940	10	7½	120'	30'	1	17	Otis	4	Yes	Yes	3-5	10-15	23	Best pavement of Otis this age
53	11	1938	8	6	202'8"	25'4"	5	17	Otis	3	Yes	Yes	5-7	50-100	25	Very poor

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[1] Only a few typical sections.
[2] County number.
[3] Pavement Index card number.
[4] On 10 percent or more all joints and cracks.
[5] Full width, concrete or bituminous.
[6] Based on reports on many projects.
[7] Typical projects—many others checked. 1938 pavement showed no cracks or patching in 1957.

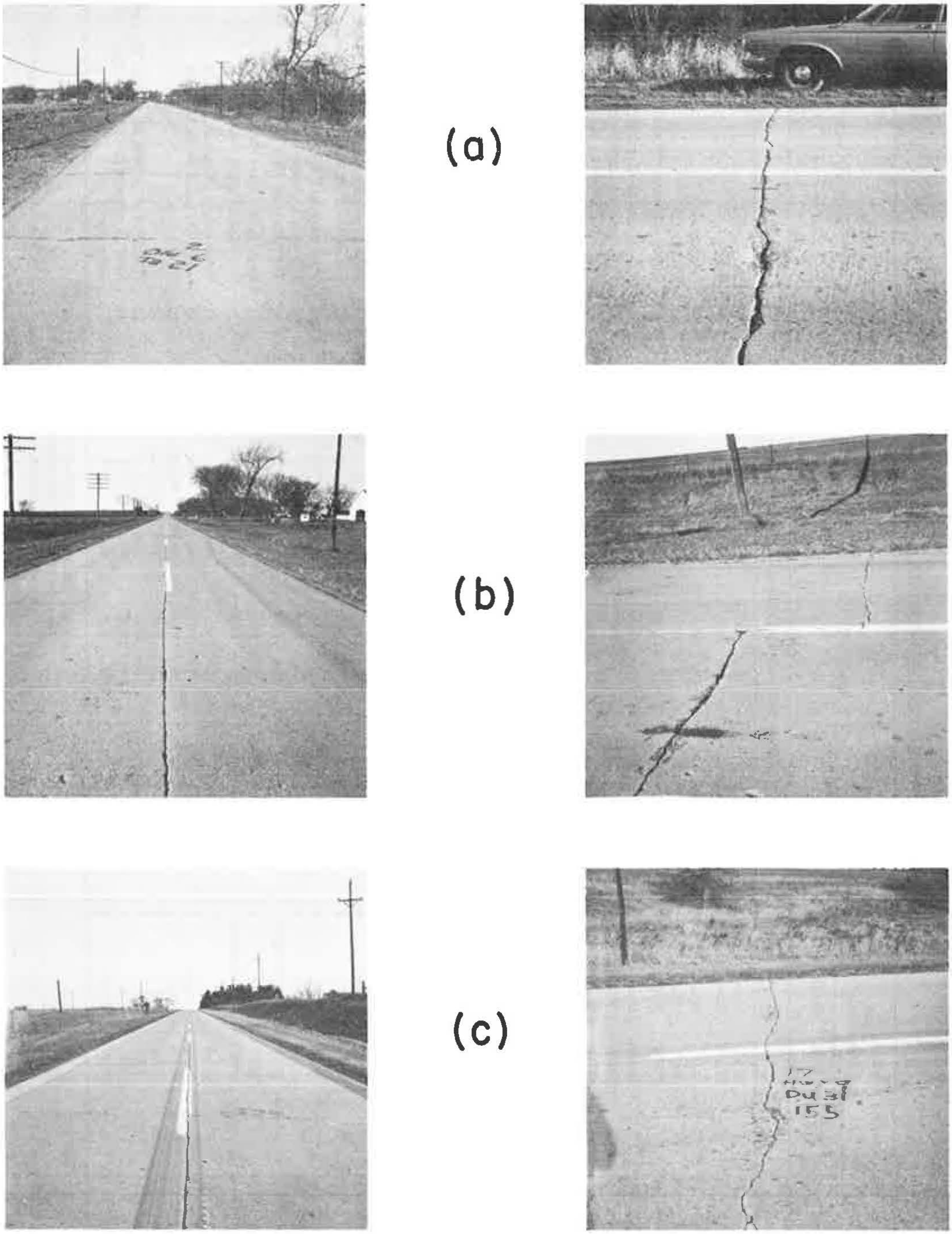

Figure 1. Concrete pavements with satisfactory service: (a) project 52-7, 42 years old, Iowa City stone; (b) project 52-5, 36 years old, Davenport stone; and (c) project 3-4, 32 years old, Dubuque stone.

oration. Some patching has been necessary where slabs are broken. The area of old concrete adjacent to patches 17 years old is in excellent condition.

Described in the following are five geologic sources with satisfactory service exceeding 30 years. Of these five, only the Farmington aggregate exceeds current limits of the water-alcohol freeze-thaw test.

Iowa City Stone (Devonian), Coralville Limestone Member, Cedar Valley Formation, Iowa City Area.—The rock is a medium to fine-grained limestone (classification of rock as used throughout this report is that of Pettijohn (6)) interbedded with biostromal (coral) layers, averaging 95 percent or better total carbonate. Currently the lower 26 ft of this unit is acceptable for use in concrete. The freezing and thawing test results are generally consistently within specifications, although the lithology is variable and becomes more dolomitic northwest along the outcrop belt.

Aggregate from this geologic source has been used in pavement with satisfactory results since 1921. Figure 1a shows a typical pavement constructed in 1921.

Davenport Stone (Devonian), Davenport Limestone Member, Wapsipinicon Formation, Davenport Area.—The Davenport member generally ranges from 20 to 30 ft thick and is essentially a uniform, very fine-grained, limestone averaging 95 percent or more total calcium carbonate. Figure 1b shows a typical section of 36-yr-old pavement containing this aggregate. This source has been used for aggregate since the early 1920's.

Dubuque Stone (Ordovician), Galena Formation, Dubuque Area.—The Galena formation in this area is a relatively uniform coarse-grained massive dolomite with a varying amount of white chert nodules scattered throughout the unit. The carbonate content of the chert-free rock is usually more than 95 percent. Working faces in this ledge vary from 40 to more than 100 ft in thickness. Concrete made with this aggregate has performed well for 35 years (Fig. 1c). Some pavements more than 35 years old are beginning to show signs of progressive deterioration but not at the same rate or to the same degree as that shown by pavements containing unsatisfactory aggregates.

Alden Stone (Mississippian), Gilmore City Formation, Alden Area.—The rock is coarsely crystalline, oolitic to crinoidal, limestone averaging 97 to 98 percent calcium carbonate. About 30 ft in the upper part of the formation have been worked at Alden. Aggregates have been produced from various horizons within the formation at Humboldt, Rutland, and Gilmore City. Some pavements up to 40 years old, containing this aggregate, have been checked, and generally the concrete is in excellent condition. Several sections more than 35 years old have only one or two patches in several miles of pavement.

Farmington Stone (Mississippian), St. Genevieve Formation, Farmington Area.—The 8- to 12-ft working face is very fine-grained limestone with thin shale partings and variable but generally thin, argillaceous limestone layers, with a variable carbonate content. Aggregate from this source exceeds present allowable loss limits on freezing and thawing in water-alcohol, but produces satisfactory concrete. Thirty-five-year-old concrete containing this stone is in excellent condition.

UNSATISFACTORY SERVICE

In this category the case histories of aggregates from five geologic sources (Glory, Fayette, Decorah, LeGrand, and Otis) are described. The Glory and Fayette sources do not meet current test requirements. Service records of these two are described to illustrate the similarities in the pattern of deterioration shown by concrete containing aggregates with different lithologies and physical properties.

For concrete containing aggregate from each of the five sources described, deterioration has been observed on at least one project where adjoining sections of pavement were constructed with concrete containing coarse aggregates from several satisfactory sources. For each section of pavement, site conditions are similar; sand, cement, and design were identical but the coarse aggregate was changed. In each project the deteriorated areas of pavement correlated with the suspect coarse aggregate. The other sections of pavement containing satisfactory aggregates remained in excellent condition. All observed concrete pavements more than 15 years of age, containing aggregates from any one of the five unsatisfactory sources, show deterioration.

General Pattern of Deterioration

The general pattern of deterioration, at whatever age it begins, is similar for aggregates meeting and for those failing to meet specifications. Significant variations are noted in the age at which deterioration is first observed, the rate at which it progresses, and the area of slab affected. Deterioration in all cases is progressive. The first noticeable sign is a general discoloration in the vicinity of the joints and cracks, and sometimes along the edges of the slab. The border of the discolored area is generally slightly concave toward the long axis of the crack or joint (Fig. 3c, left).

"D" line cracking, the next sign of deterioration, is a network of fine, parallel, hairline cracks which generally develop on both sides of a joint or fracture before progressive scaling is observed. These fine cracks parallel the joints, fractures or edges, usually curve across slab corners and are interconnected by random transverse cracks (Figs. 3c, right and 6b). Sometimes these cracks accumulate a small, light blue-gray, ridge-like deposit and are referred to as "blue-line" cracks. Within the cracked area, the surface layer of concrete from ⅛ to ¼ in. thick is loosened and is easily peeled from the slab. Discoloration generally continues to spread ahead of the "D" line cracking.

The deteriorated area is deepened by progressive scaling (Fig. 6d). The concrete in these areas is easily disintegrated by a light hammer blow. The matrix is generally chalky, and cavity walls may be coated with a white powder. This material has been identified by Lemish (1) to be predominantly calcium carbonate. During the early stages of deterioration, the central portion of the slab (Fig. 3) between cracks or joints shows no indication of distress. In extreme cases the entire slab may be affected (Fig. 2). In the final stage the concrete deteriorates to a condition resembling loosely compacted gravel. Any one pavement will generally show all degrees of deterioration. Variations in the severity of deterioration are greater in a horizontal direction away from joints and cracks than from top to bottom in the vicinity of joints or cracks.

On pavement with transverse joints, deterioration appears to start adjacent to the expansion joints, then the contraction joints and finally develop adjacent to the cracks. With time, progressively more area of the pavement is affected. In most instances there does not appear to be any obvious displacement of the pavement in the deteriorated areas.

The general pattern does not appear to be similar to that described and illustrated by Swenson and Gillott (2) in Canada or by Newlon and Sherwood (3) in Virginia. It appears to be similar to that described and illustrated by White and Peyton (4) in Kansas and Woods et al. (5) in Indiana.

Blow-ups or eruptions of the concrete similar to that illustrated in Figure 7c (left) have been observed on pavements containing both satisfactory and unsatisfactory aggregates. These eruptions may be caused by any number of factors and may or may not be related to the properties of the coarse aggregate. Once an area has been patched it is difficult to determine the reason for the failure.

Described in the following are the case histories for five unsatisfactory aggregate sources.

Glory Stone (Devonian), Rapid Member, Cedar Valley Formation, Waterloo to Davenport. —The Rapid member is a fine- to medium-grained, blue-gray, argillaceous, cherty, dolomitic limestone that may be massive or laminated, generally containing less than 90 percent carbonate.

The Rapid member occurs in many of the quarries where acceptable stone has been quarried separately from the overlying Coralville member and is the most widely studied geologic material in Iowa associated with concrete deterioration. Aggregate from the Rapid member consistently exceeds freeze-thaw test limits.

Deterioration of concrete containing aggregate from the Rapid member was first recognized in eastern Iowa early in 1930. This rock was not used again in that area. However, because the geologic correlation was not established for all the quarries in the outcrop belt, the rock was eliminated in some quarries and not in others. Deterioration was later associated with this same layer of rock for aggregate from the Glory quarry.

Between 1927 and 1934 aggregate from the Glory quarry was used in many paving projects in northeast Iowa. In nearly every case the pavement began to show signs of deterioration at ages ranging from 3 to 8 years. By 1950 nearly all the pavement made with Glory aggregate was in a critical state of deterioration. Figure 2 shows the appearance of typical sections of pavement containing aggregate produced from the Rapid member. Aggregate from this kind of rock is usually referred to as Glory type because of the association with the Glory quarry.

The 40-ft working face at the Glory quarry has up to 10 ft of the Coralville member overlying 30 ft of the Rapid member. The Coralville member is a fine-grained limestone containing 95 percent or more calcium carbonate. This quarry face is duplicated almost exactly at Pints quarry. Rock from Pints quarry has been used in these studies because no material has been produced from the Glory quarry for many years.

Test results on separate samples of aggregate from the Coralville or Rapid members are usually consistent. Rock from the Coralville member meets, but rock from the

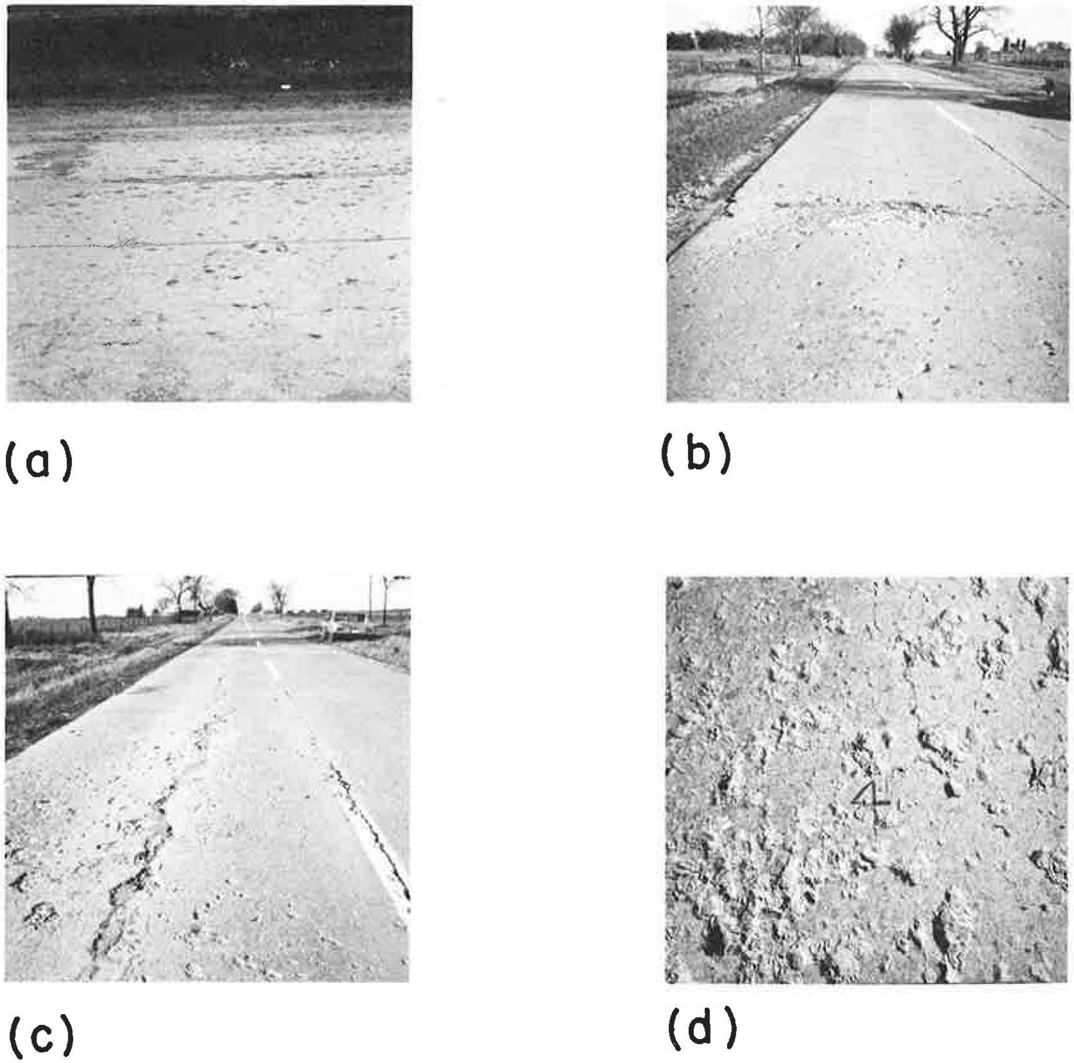

Figure 2. Typical condition of concrete containing aggregate from the Rapid member: (d) is close-up of area shown in (c).

Rapid member exceeds the freeze-thaw test limits. Test results on the crushed product are highly variable whenever stone from both members is present in the samples tested.

Glory type aggregate has been studied extensively by Lemish et al. (1, 7, 8, 9, 10). This was the rock in which Lemish (7) noted the presence of peripheral rims in the coarse aggregate particles taken from deteriorated concrete.

The Rapid also has an effect on the durability of concrete when mixed with aggregates that have shown 40 years of excellent service when used separately. Occasionally aggregate from the Iowa City quarries included variable amounts for the Rapid member wherever quarry operations extended deeper than the Coralville member. In one paving project variable amounts of aggregate from the Rapid member were included in the aggregate used in some randomly located areas of concrete, that is now 37 years old. Wherever the concrete shows deterioration, as in Figure 2b, it is almost always possible to find the characteristic blue-gray aggregate particles of Rapid member. For sections of pavement in excellent condition, few or no particles are found that are similar in lithology to the rock from the Rapid member. There appears to be a correlation between the amount of Rapid visible in the concrete and the extent of the deterioration. More work will be needed to verify this relationship.

Fayette Stone (Devonian), Solon Member, Cedar Valley Formation, Davenport and Spring Grove Members, Wapsipinicon Formation, Fayette Area.—Aggregate from the Fayette quarry was used from the late 1920's to the early 1940's. The upper part of the section in this quarry is assigned to the Solon member of the Cedar Valley formation, and the lower part to the Davenport and Spring Grove members of the Wapsipinicon formation. At this quarry the Solon member is an argillaceous, slightly dolomitic limestone similar in lithology to the rock of the Rapid member. The Davenport member at this quarry is of much poorer quality than at some other localities. The Spring Grove member is a laminated, high calcium carbonate limestone with a low percent of loss in the freeze-thaw test. The rock that was quarried at the time aggregates were produced for concrete was generally a mixture of varying amounts of Solon, Davenport, and Spring Grove members. Although the average quality of the rock as measured by the water-alcohol freeze-and-thaw test is slightly better than the material from the Glory quarry, it is still outside currently acceptable limits.

Pavement, made with Fayette stone, remains in excellent condition without any signs of deterioration for at least 20 years. Sometime between 20 and 25 years of age deterioration begins and progresses very rapidly. Figure 3 shows the general condition in 1963 of highways ranging in age from 23 to 27 years. Table 3 shows that most of the 23-yr-old pavement has only a few patches, whereas the number of patches increases very rapidly for progressively older pavements. Several of the projects in Table 3 have been under observation since 1957. In 1957 the concrete on project 28-11 was in excellent condition. Photographs of this project taken in 1958 are shown in Figure 4. In 1960 this pavement appeared similar to that in Figure 3c with several patches per mile. By the fall of 1963 deterioration had progressed in the original concrete adjacent to the older patches and the number of patches per mile has greatly increased.

Unsatisfactory Service but Meeting Test Limits

Although there is interest in the mechanics of the failure associated with the lithologies shown by the Rapid and Solon members, this rock is not a problem at this time. Rocks of this type, the argillaceous limestones and dolomitic limestones, are eliminated by the six percent maximum allowable loss in the current water-alcohol freeze-thaw test.

Presently the problem concerns three relatively pure carbonate aggregates, consisting of 95 percent or more total carbonate content, that meet all current test requirements, but give unsatisfactory service and have no known or currently measurable characteristics to differentiate them from the aggregates with good service records. Two of these sources, Decorah and LeGrand rocks, have been rejected on the basis of service record. Concrete containing aggregate from the Otis member is deteriorating very rapidly in pavements less than 20 years old.

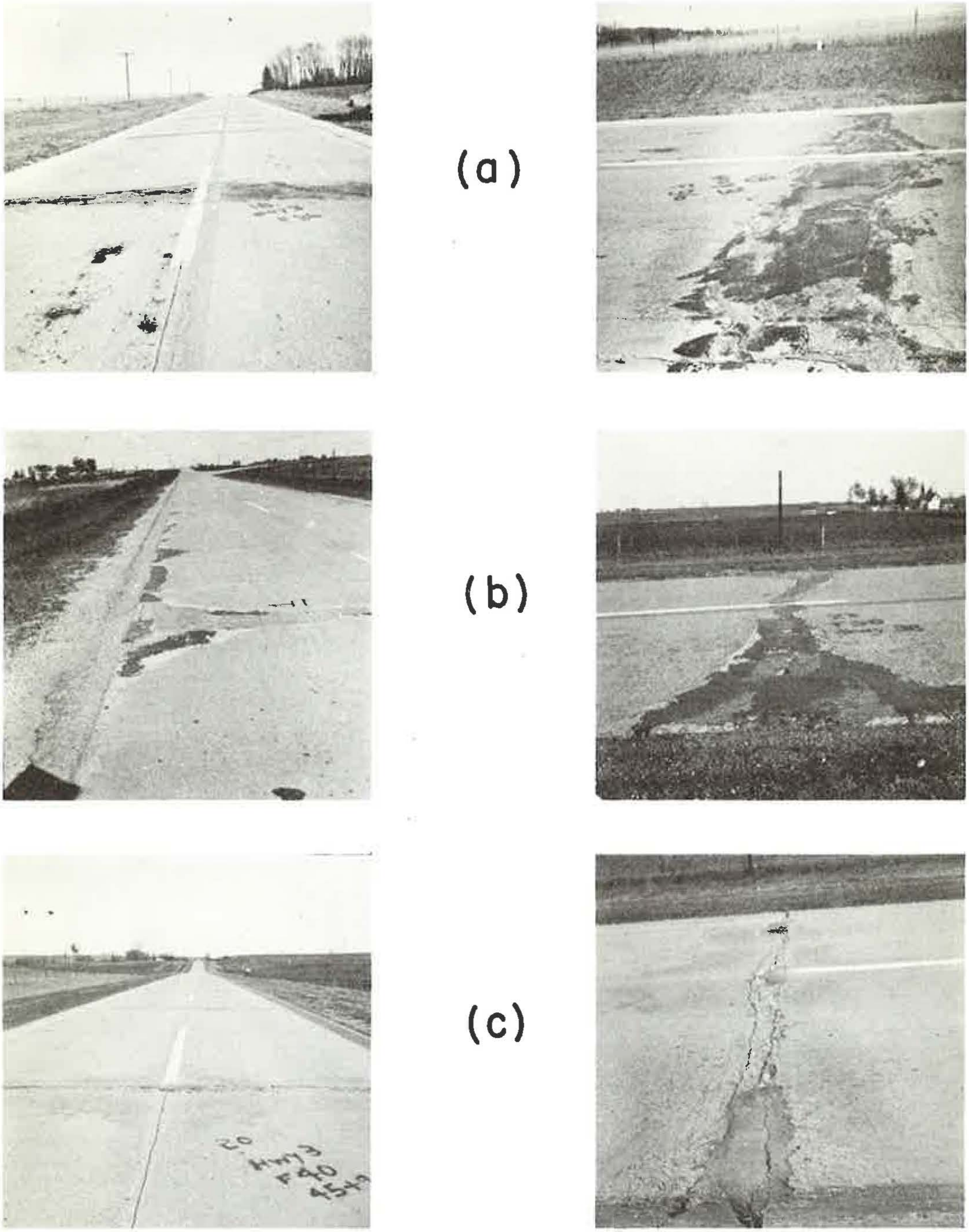

Figure 3. Typical condition of concretes of various ages containing Fayette stone: (a) project 28-10, 27 years old; (b) project 28-11, 24 years old; and (c) project 28-14, 23 years old.

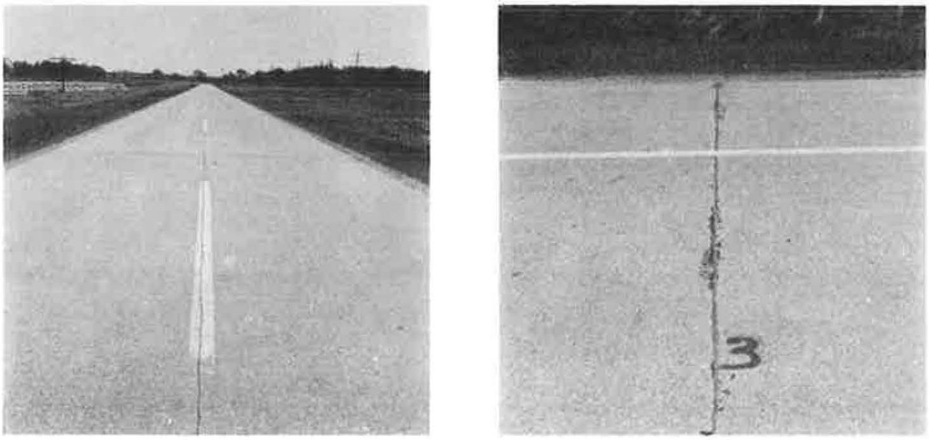

Figure 4. Project 28-11 in 1958, 20 years old. Compare with Figure 3b (left).

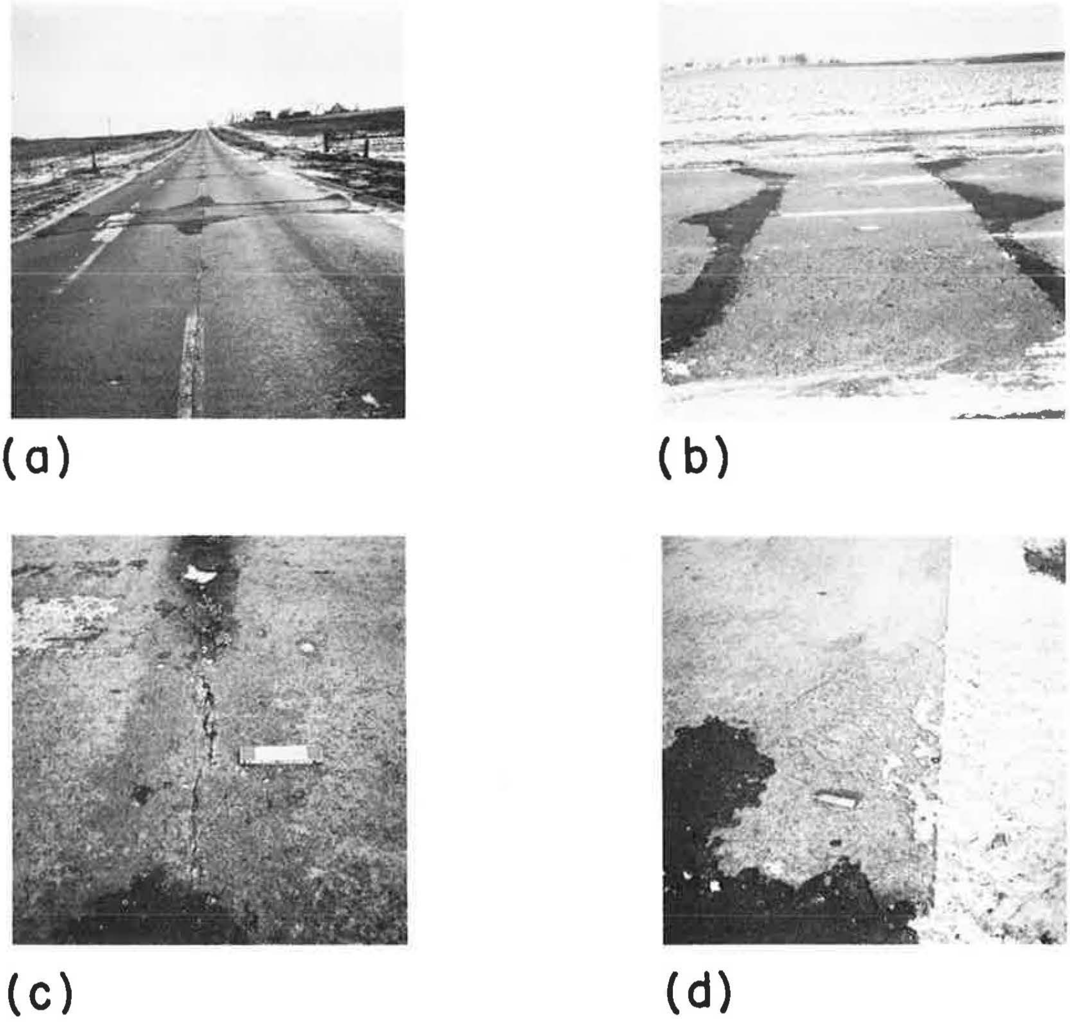

Figure 5. Typical condition of concrete containing LeGrand stone, project 85-11.

LeGrand Stone (Mississippian), Maynes Creek Member, Hampton Formation, LeGrand Area. —In general, the rock is a medium-grained, crinoidal, variably weathered, cherty, dolomitic limestone with induration ranging from hard and dense to soft, porous and friable. The total carbonate content of the chert-free rock averages about 95 percent.

The LeGrand aggregate was the first aggregate meeting test limits to be associated with early concrete deterioration. The rock was used extensively from the late 1920's to the late 1930's. Deterioration of the concrete did not appear as early as with Glory aggregate. Generally, deterioration was first noted when the pavements were about 10 years old and became severe when the concrete was between 15 and 20 years of age. The general pattern of deterioration (Fig. 5) is much the same as that seen on pavements containing Glory aggregate. Photographs (Fig. 5) were taken in 1963 of 25-yr-old pavement that has more than 500 patches in five miles.

Decorah Stone (Ordovician), Galena Formation, Decorah Area. —The rock is medium-grained limestone mottled with soft patches of dolomite, averaging about 95 percent total carbonate. Working faces in the quarries ranged from about 30 to more than 100 ft in height. In general, these faces are fairly uniform in lithology and comply with specifications test limits on a bed-by-bed basis.

The quarries in the Decorah area are in approximately the same stratigraphic horizon as those at Dubuque. Test results are very similar for aggregate from the Dubuque and Decorah sources. The most obvious difference is the lower MgO content of the Decorah rock although the total carbonate content is similar. Aggregate from the Decorah quarries was used in the late 1920's and early 1930's. In 1960 an investigation was made to determine the service record of the concrete made with this rock.

Pavements containing Decorah aggregate that were examined were from 28 to 30 years old. These were compared with pavements of similar age, in the Decorah area, that contained coarse aggregates with satisfactory service records. For several projects, Decorah aggregate and coarse aggregates from one or more other satisfactory sources were used separately for concrete in adjoining sections of pavement. Concrete containing Decorah aggregate was compared with that containing Dubuque crushed stone and Mason City crushed stone. In all projects the concrete with Decorah aggregate showed extensive deterioration. Typical sections of pavements containing Decorah aggregate are shown in Figure 6. The number of patches per mile varies from 30 to more than 150 for various projects under investigation. Concretes containing the other aggregates were in excellent condition. Compare patch counts for projects 3-4, and 96-18 in Table 3. These are adjoining projects on the same highway. The views in Figure 1c were taken on project 3-4, a few hundred feet west of the area shown in Figure 6.

Records of crack surveys made in 1944 of pavement containing Decorah aggregate indicated that deterioration was first noticed when the pavements were about 14 years old.

Otis Stone (Devonian), Otis Member, Wapsipinicon Formation, Cedar Rapids Area. —This geologic source is the most recent to be suspected of being directly related to early pavement deterioration.

The unit ranges from 20 to 25 ft in thickness and consists of alternating beds of fine and medium to coarse-grained rock that varies from dolomite limestone to calcitic dolomite and contains more than 96 percent total carbonate. Each ledge in the quarry face used for concrete meets the test requirements of the specifications.

Deterioration was first noticed in 1958 on pavements ranging from 14 to 20 years of age. In 1957 and 1958 the condition of most Otis pavement was similar to that tabulated for project 28-17 (Table 3). Joints showed evidence of spalling near the quarter point and one to two joints per mile had been patched. Some discoloration was noted but no "D" cracks were seen. During the next few years periodic observations were made of many sections of Otis pavement ranging from 5 to 23 years of age. Deterioration of varying severity was noted in all pavements exceeding 14 years of age. In general, deterioration was more severe on pavements more than 16 years of age. Photographs taken in 1963 of several pavements containing this aggregate are shown in Figure 7. These pictures show the typical but variable pattern of increasing deterioration and patching with increasing age beyond 15 years. Some failures (Fig. 7c, left) were noticed where there appears to be displacement of the concrete.

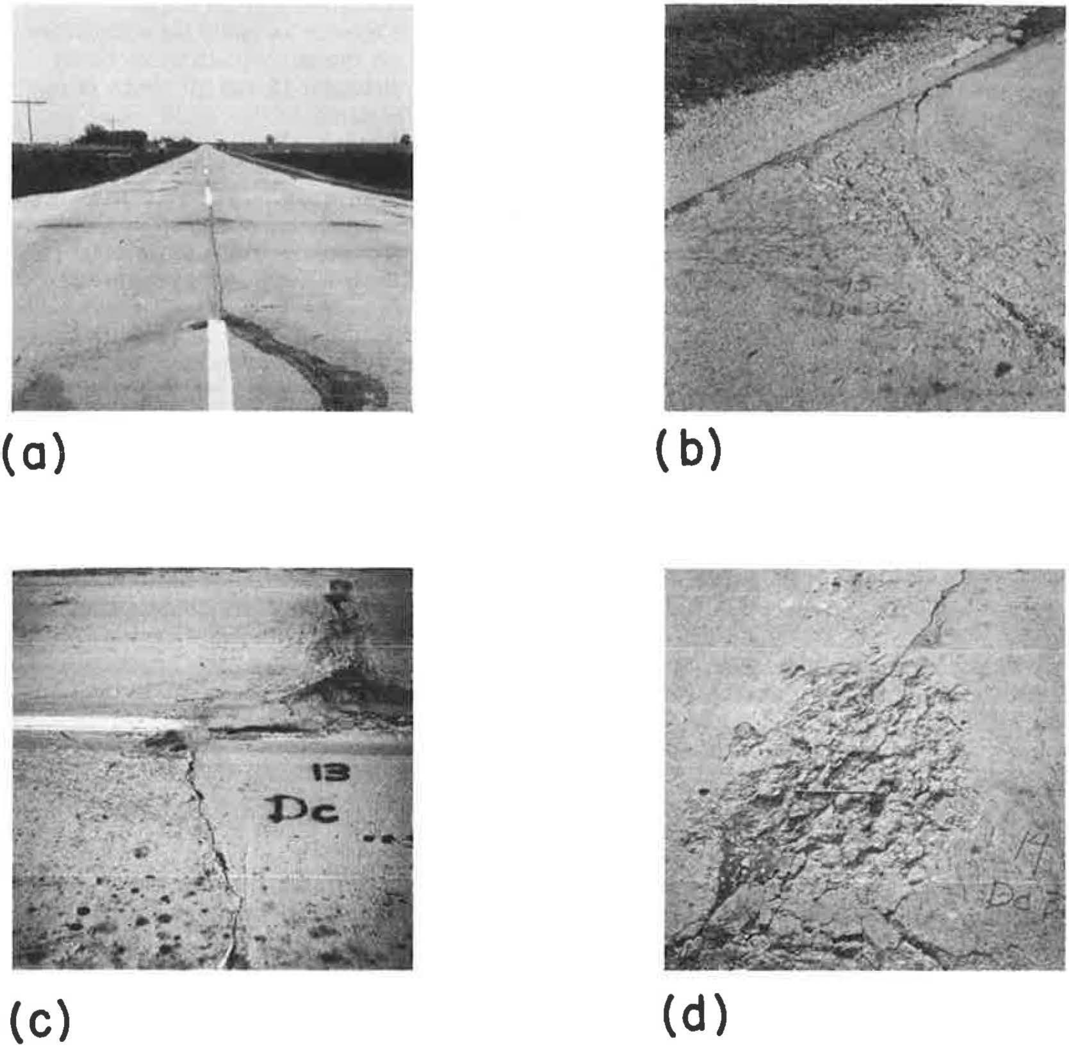

Figure 6. Typical condition of concrete containing Decorah stone, project 96-18.

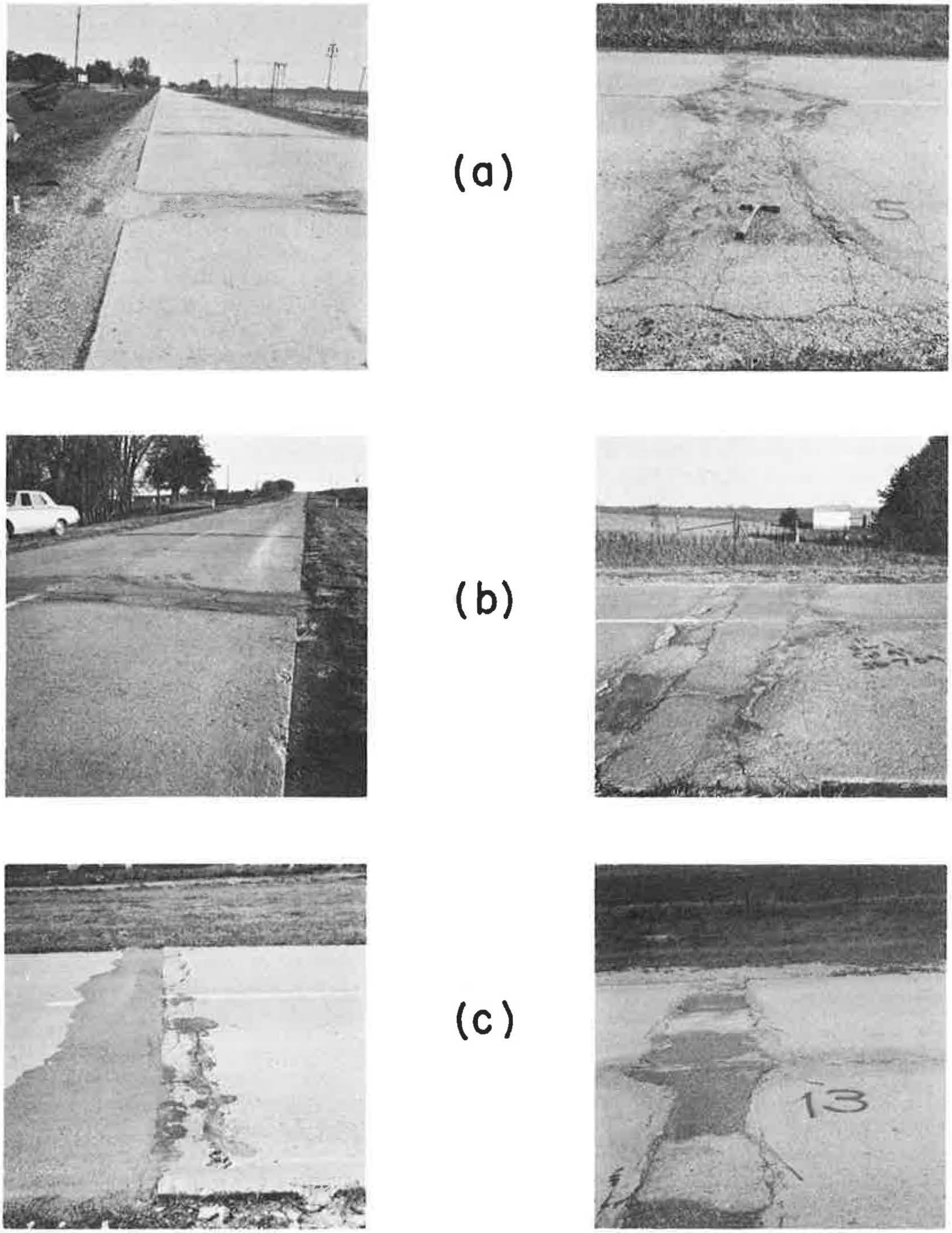

Figure 7. Typical condition of concrete of various ages containing Otis stone: (a) project 53-11, 25 years old; (b) project 52-25, 22 years old; and (c) project 57-38, 18 years old.

ROCK PROPERTIES STUDY

It is not within the scope of this paper to go into the details of testing procedure or to tabulate the numerous test results that have been obtained on a wide variety of rocks currently being studied, other than those given in Tables 4 and 5. Other test results can be found in publications referred to throughout the text. Current studies include routine tests, conducted by the Highway Commission, and special studies being made under separate research projects by Lemish, and Biggs, at the Geology Department, Iowa State University. Routine tests include the Los Angeles abrasion, freezing and thawing in water-alcohol solution, chemical analyses, and sometimes X-ray studies. Special studies of the carbonate rock at Iowa State University include calcite dolomite distribution, variations in carbonate mineral composition, physical property determinations, specific gravity, absorption, porosity, permeability, specific surface, pore size distribution, determination of insoluble residue, petrographic studies, and rock expansion studies.

Although all tests are conducted on a ledge-by-ledge basis for each quarry the data given in Table 4 are averages for the face worked concrete. Where ledges with significantly different properties are used, each ledge is tabulated separately.

Table 4 shows that unsatisfactory aggregates that exceed 6 percent loss on the freeze-thaw test, range from limestone to calcitic dolomite and contain more than five percent insoluble residue. The residue is generally silt and clay-size quartz and illitic clay. Rocks in this group have freezing-and-thawing losses as high as 60 percent. Lemish (7) initially demonstrated that the greater the insoluble residue content in excess of five percent, the higher the loss on the water-alcohol freezing-and-thawing test. Subsequent testing carried on at the laboratory of ISHC on hundreds of samples has verified this relationship. The relationship does not always hold true when the insoluble residue is chert or sand-sized quartz grains.

Table 5 shows that some of the Glory rock has properties similar to expanding rocks described as occurring elsewhere in the United States and Canada (2, 3, 12), that are associated with the alkali-carbonate rock reaction.

The LeGrand, Decorah and Otis rocks associated with deterioration have measurable properties that are similar to rocks with satisfactory service. They are usually within the allowable six percent freeze-thaw loss, average less than five percent insoluble residue, have little or no illitic clay, and show a variety of lithologies. One characteristic that all three have in common is an intermediate MgO content, ranging from about 5 to 15 percent. However, there is one other aggregate source (Ferguson) with a similar composition that appears to give satisfactory service. Studies by Lemish (11) indicate that these rocks either show no length change or shrink when soaked in alkali solution (Table 5).

Sodium sulfate soundness test results in Table 4 do not appear to have any correlation with service record or the Method "A" freezing-and-thawing test.

CONCRETE STUDIES

The same carbonate aggregates that are being studied for rock characteristics have been and are currently being studied in concrete specimens, in various test environments, and in the concrete pavement. Some phases of the study have been completed and found to be inconclusive by themselves when run on a concrete containing one or another of a wide variety of satisfactory and unsatisfactory aggregate. These tests may have more significance when analyzed in terms of rock characteristics.

Aggregates from more than 25 sources have been used in making 4- by 4- by 18-in. beams for long-time outside storage and for use in the automatic freezer, ASTM method C291-61T, and for special wetting, drying, heating and cooling tests. Cylinders have been made for 3-yr strength studies (Table 4). Special tests for alkali reactivity have been run on mortar bars according to ASTM method C227-52T. Gage plugs have been set in various pavements to study growth. To date, the characteristics measured by these tests have not shown any definite limits that are not present to the same degree in concrete containing one or another of the satisfactory aggregates.

TABLE 4

ROCK PROPERTIES AND CONCRETE TESTS

Source	Soundness Loss (%)		LA[2]	Sp. Gr.	Abs. (%)	Typical Chemical Analysis (%)						Insol. (%)	Conc. Compr. (psi)		
	NaSO₄	"A"				CaO	MgO	Loss	Fe_2O_3	Al_2O_3	SiO_2		28 Day	1 Yr	3 Yr
(a) Satisfactory Performance															
Alden	26.9	1.2	41	2.56	1.83	54	1	43	0.1	—	1.0	0.4	5,558	6,378	NC[3]
Dubuque	22.3	2.7	34	2.72	1.08	30	19	44	0.4	0.5	5.0	5.0	5,328	6,172	7,165
Iowa City[4,5]		2.3	32	2.64	1.03	49	4	43	0.1	2.0	0.7	2.0	4,815	5,978	7,043
Davenport[5,6]		1.6	32	2.68		52	2	44	—	—	1.0		5,275	6,125	6,285
Farmington	19.6	8.0	25	2.69	0.63	49	2	41	—	0.6	5.6	5.3	5,151	6,133	6,224
Ferguson	18.6	1.7	36	2.69	1.70	39	12	45	0.9	0.4	1.9	2.0	5,385	6,378	6,790
(b) Unsatisfactory Performance															
Decorah		1.2	35	2.74	0.70	41	11	44	0.3	0.7	2.4		5,160	6,584	NC[3]
Otis[5]	15.5	1.8	33	2.68	1.35	34	16	45	0.6	0.6	1.8	1.2	5,537	6,821	7,030
LeGrand[5]	25.9	3.8	36	2.65	0.95	45	7	43	0.3	0.5	3.3	3.4	5,572	6,748	NC[3]
Fayette															
Solon		20.4	30			51	0	41	0.6	3.3	3.3				
Davenport		41.0	48			50	0	40	0.7	3.2	4.6				
Sp. Grove		2.3	34			53	0	43	0.3	0.5	1.7				
Glory quarry[5]															
Coralville		1.8	30			56	0	41	0.1	0.2	0.4				
Rapid		30.0	34			30	15	40	0.7	2.0	11.1	14.0			
Pints[7]	31.1	16.0	32	2.58	3.65	28	15	39	2.0	1.1	13.1	17.0	5,682	5,911	
Iowa City[4,5]															
Rapid		60.0	43			28	15	39	2.0	1.1	13.3	13.0			

[1] 16 cycles freezing and thawing in water-alcohol.
[2] Los Angeles abrasion test.
[3] Not completed as of Jan. 1964.
[4] River Products quarry.
[5] Quarries studied by Lemish (11).
[6] Linwood quarry.
[7] Same horizons as Glory quarry.

Lemish (11) has undertaken a systematic study of cores from concrete pavements of various ages containing one or another of coarse aggregates from different sources to learn more about changes in the concrete system with time. Aggregate particles are being studied petrographically in concrete beams after testing and in cores from concrete pavements of various ages and conditions to determine, if possible, what changes are taking place and if these changes are different for different aggregates.

Compressive Strength of Pavements

Compressive strengths of cores taken taken in 1963 from 15 projects representing aggregates from six different geological sources are given in Table 6. All cores were taken from the sound portion of the pavement. No relation between condition and strength is apparent.

TABLE 5

EXPANSION DATA AND ANALYSES OF ROCK PRIOR TO ALKALI TREATMENT[1]

Quarry	Bed	Residue Wt. (%)	Ca, as $CaCO_3$ (% wt.)	Mg, as $MgCO_3$ (% wt.)	Si, as SiO_2 (% wt.)	Expansion[2] (%)
Dubuque	1	3.5	92.9	3.0	3.1	- 0.1
	3	15.5	45.0	38.8	12.9	- 0.2
	4	3.3	51.6	44.3	2.3	- 0.2
Ferguson	2	1.8	89.3	9.0	1.7	- 0.1
	4	7.1	52.6	38.6	5.2	- 0.1
	6	0.8	93.8	5.3	0.6	- 0.1
	7	11.2	50.6	36.1	7.5	0.1
	9	1.6	71.3	23.9	0.4	- 0.2
	10	2.7	63.0	33.2	2.1	- 0.1
	11	3.2	62.0	33.4	2.1	- 0.1
	12	1.9	95.1	2.2	1.7	- 0.1
	13	2.8	64.8	31.2	1.9	- 0.1
	14	1.4	78.8	18.3	1.1	- 0.1
	16	1.3	89.0	8.6	1.7	- 0.2
	17	1.4	78.3	19.1	1.7	- 0.2
	19	1.9	59.9	36.5	1.2	- 0.2
Glory	2	7.2	66.5	24.8	5.2	0.8
	3	10.1	65.2	23.4	6.8	1.2
	4	10.9	60.9	26.1	7.5	0.4
	5	12.1	61.9	23.9	8.6	1.1
	6	12.8	62.9	22.1	9.2	0.8
	8	9.1	68.4	20.7	6.9	0.2
	9	15.9	53.3	28.4	11.2	0.0
	10	16.1	50.3	31.5	11.7	0.1
LeGrand	8	2.7	57.4	37.7	1.9	0.0
	9	2.6	56.1	39.0	1.9	0.0
	10	1.6	70.3	26.3	1.5	0.0
	11	1.6	64.1	31.9	1.6	0.0
	12	2.0	62.0	34.1	1.7	0.0
	13	1.0	82.0	15.0	1.3	0.0
Linwood	3	0.4	97.0	1.9	0.6	- 0.1
	4	0.8	98.3	0.4	0.7	- 0.1
	6	0.7	97.1	1.6	0.3	- 0.1
	9	1.2	96.8	1.6	0.9	- 0.2

[1] Partial table: Lemish and Moore (11).
[2] 150 days in NaOH.

TABLE 6

COMPRESSIVE STRENGTHS OF CORES FROM CONCRETE PAVEMENTS

Project		Coarse Aggregate	Sand	Cement	Age (yr)	Avg.[1] (psi)
Co.	Cd.					
(a) Satisfactory Performance						
40	13	Alden	20	2	27	7,462
85[2]	5	Alden	1	1	34	7,805
31	26	Dubuque	4	5	6	8,137
31[2]	13	Dubuque	4	4	31	10,080
31		Dubuque	4	3	35	10,797
31	2	Dubuque	4	5	36	10,982
52[2]	2	Iowa City	5	4	42	6,940
52[2]	7	Iowa City	6	5	36	8,616
(b) Unsatisfactory Performance						
96	6	Decorah	21	5	35	9,761
57	64	Otis	17	5, 7, 4	2	7,136
57	60A	Otis	17	5	7	8,430
57	54	Otis	17	5	11	8,230
57[2]	38	Otis	17	5	17	9,698
52	26	Otis	17	2	22	10,000
53[2]	11	Otis	17	5	25	8,627

[1] Avg. 3 or 4 cores, generally less than 500-psi variation.

[2] Also in Table 3.

DISCUSSION

From service record studies, it is found that most of the concrete containing carbonate aggregates that meet current test limits can be expected to remain durable for 25 to 30 years. Deterioration of concrete with less than 20 years of service has been associated with the five sources in this report. For each of these sources an age span can be assigned at which the first signs of deterioration in the concrete are noticeable, even with variations in design, cement, sand, foundation conditions, and traffic. These are Glory, 3-5 years; Fayette, 20-23 years; LeGrand, 10-14 years; Decorah, 12-16 years; and Otis, 14-17 years. In all cases the pattern of deterioration is similar and progressive with disintegration throughout the entire pavement containing the unsatisfactory aggregates, when the concrete is about 25 to 30 years of age.

In general, the six percent loss limit on the water-alcohol test shows a good correlation between performance and test results for about 40 geologic sources. The Farmington aggregate is the exception, it averages eight percent loss but has a 35-year satisfactory service record. The other seven sources that exceed the six percent loss, like Glory and Fayette, have unsatisfactory service records. However, this freeze-thaw test and other test procedures that have been tried do not show any properties to separate the unsatisfactory LeGrand, Decorah, and Otis aggregates which meet test limits from aggregates with satisfactory service. This would indicate that there are other properties or combinations of properties not being measured that affect the durability of the concrete.

It is hoped that the research studies now in progress will show a measurable property or combination of properties that will establish a better correlation between test results and concrete durability.

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Part III. REGIONAL STUDIES

Expansion of Gull River Carbonate Rocks in Sodium Hydroxide

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•THE ALKALI-CARBONATE rock reaction that has caused serious deterioration of concrete (Fig. 1) appears to be limited in Ontario to rocks of the Gull River formation. This Middle Ordovician formation, which occurs in a narrow zone averaging about 10 mi wide along the southern border of the Canadian Shield, was formerly known as the Black River formation but was redefined by Liberty (6) on the basis of lithological characteristics.

Because many quarries (5), among them the classical Kingston quarries, are located in this formation, an investigation was conducted to establish whether the expansive type of rock found at Kingston occurs elsewhere in Ontario and, if so, whether it might be used by Ontario Hydro as concrete aggregate.

MATERIALS AND METHODS

Sampling

More than 200 samples were collected from 18 locations in the Gull River formation. The locations sampled in the 200-mi stretch from Georgian Bay to Kingston (Fig. 2) included eight operating quarries, four abandoned ones, and three highway cuts. The sampling extended to three locations of the Black River group (Adirondack Sheet, 1) south of the Canadian border. For comparison, a few carbonate rock samples from the overlying Bobcaygeon formation were included in the program, as well as 39 carbonate particles from two gravel pits outside the Gull River formation.

The samples were taken from the different megascopically distinguishable rock varieties occurring in the various locations. Most of the specimens used in this study were fresh and by normal evaluation techniques would be considered satisfactory for use as concrete aggregates.

Test Method

For convenience, the samples were tested for expansion in NaOH solution rather than in concrete. However, instead of large prisms ($1\frac{1}{2}$ by $5\frac{3}{4}$ in.) as used by Swenson and Gillott (8), or small prisms ($\frac{1}{4}$ by $1\frac{1}{4}$ in.) as adopted by Hadley (4), small cylinders $\frac{5}{16}$ in. in diameter and $1\frac{1}{4}$ in. in length were used. These cylinders were cut with a diamond drill from the rock samples at right angles to the sedimentation layers, if possible. The cylinders were cut to the required length and the ends were shaped conically by means of a jig and a normal grinding lap (Fig. 3); the length of the cylinders

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wk, after which the length of the cylinders either remained more or less constant or increased at a very slow rate.

3. Late-major-expansion group—expansion of at least 0.40 percent, starting to expand after 25 wk (in one case after more than 1 yr) and continuing to expand for the full testing period.

Rocks classified in the late-expansion group were found to be much less common than those classified in the minor- and early-expansion groups. Only five cylinders from two locations belonged to the late-expansion group, but these specimens were sufficiently well defined by expanding characteristics and petrographic characteristics to be considered separately as a distinct group. Furthermore, whereas layers may contain expanding rocks of both the minor- and early-expansion groups, it appears that those layers containing late-expansion rocks did not contain rocks of the other two expansion groups. On the other hand, minor- and early-expansion types occurred at the same locations as late-expansion rocks but in different layers.

The late-expansion group is probably one of the causes of the irregularly occurring and seemingly delayed expansion of concrete containing expanding carbonate rocks of the Kingston type.

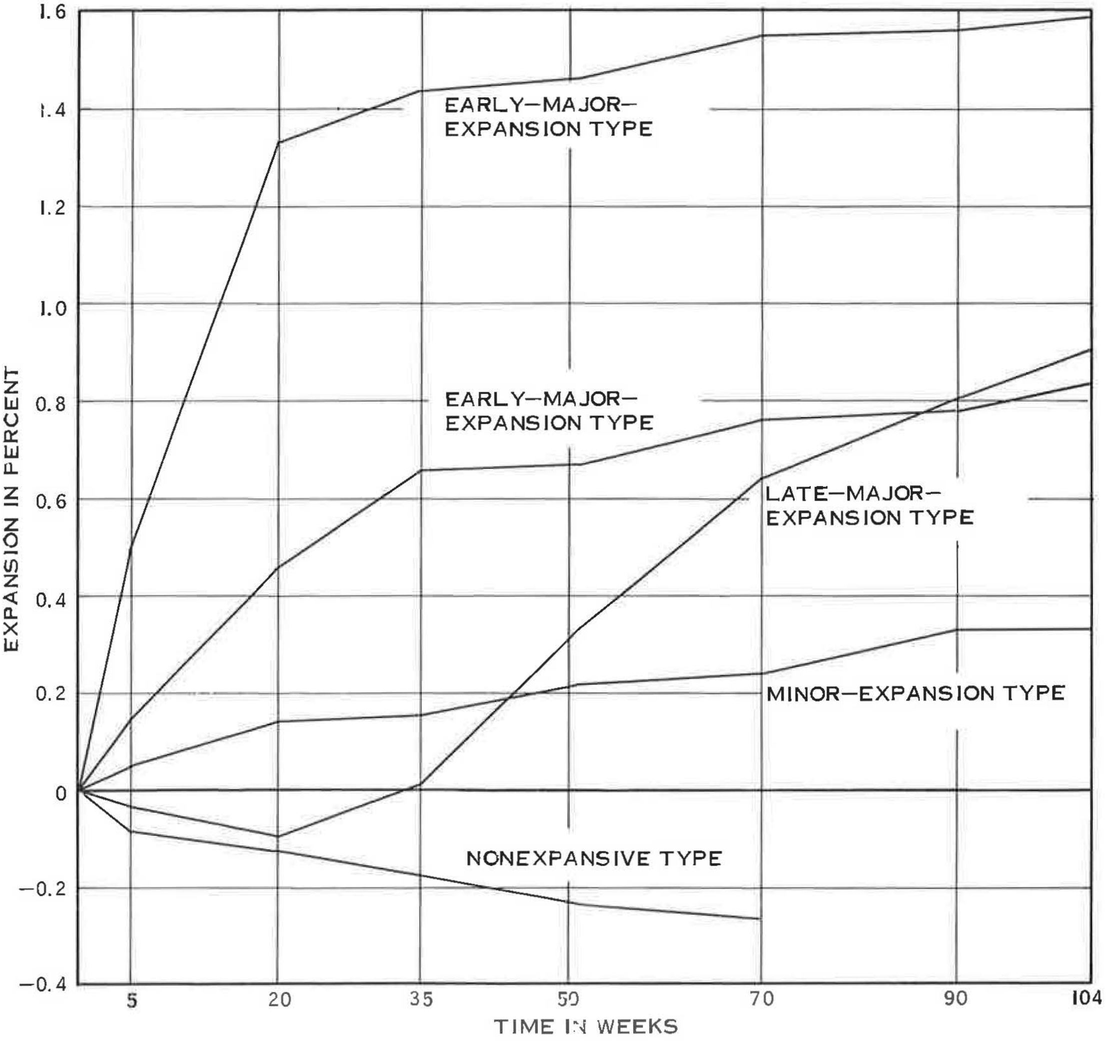

Figure 4. Expansion vs time for typical rock cylinders in NaOH immersion.

Figure 4 shows typical expansion curves of the three groups described, together with a curve characterizing the cylinders that did not expand. This graph shows the difference between the early-expansion group, which has a parabolic expansion curve, and the late-expansion group, which has a typical sigmoidal curve with negative values during the first 25 wk or more.

Many samples characterized by low expansion rates are found to have negative values at early testing ages. This phenomenon is typical for the late-major-expansion group, but shrinkage is developed most clearly in nonexpansive cylinders. The greatest decrease in length obtained in a Gull River rock was 0.26 percent for a nonexpansive cylinder having 46 percent of acid-insoluble residue. (The greatest reduction in length, 0.45 percent, was observed on a cylinder made of a Bobcaygeon rock that contained only 12 percent of noncarbonates.) The nature of these shrinkage phenomena is not known. Shrinkage could go undetected in cylinders having high early rates of expansion. If this phenomenon is a characteristic of slowly expanding cylinders only, then the expansion should be determined from the minimum length measured rather than from the length after water stabilization. However, because it could not be demonstrated that shrinkage did not occur in the early-major-expansion group, no corrections were made for the effect.

Figure 5 shows the individual curves of the major-expansion groups and a band representing the minor-expansion group. The testing of nonexpansive and some minor-expansion cylinders was terminated after 52 to 70 wk of immersion. The test results indicated that it is advisable, for full appraisal and understanding of a quarry, to continue the testing of all rocks by this method for at least 70 wk to be sure that all minor-expansion as well as late-major-expansion samples are detected.

The cylinder represented by curve 2 seems to belong to the minor-expansion group after 1 yr of testing. However, it has to be included in the late-major-expansion group because it was cut from the same rock specimen as the late-major-expansion cylinder, curve 1, and because it shows a typical expansion curve of that group. Both cylinders demonstrate the heterogeneous expansion behavior which might be encountered on small samples. An additional three samples that show more than usual differences in expansion between cylinder pairs taken from the same specimen are shown in the Appendix.

Expansion in Short-Duration Tests

The results of an attempt to predict the presence of expanding rocks in a location by their performance in NaOH solution in a relatively short-term test are shown in Figure 6, which contains the data for all expanding cylinders and for those nonexpansive cylinders which showed some expansion at the 2- and 5-wk periods but were classified as nonexpansive because they failed to reach 0.1 percent expansion during the whole testing period. The most important feature of this graph is that it shows that the late-expansion group would be completely overlooked in short-duration tests of 2 or 5 wk and might not even be recognized as a major-expansion group after 1 yr of testing.

From the limited tests carried out, it can be concluded tentatively that all cylinders showing more than 0.1 percent expansion in a 2-wk testing period belong to the early-major-expansion group, but one-third of the samples belonging to this group would not be recognized as such at the end of 2 wk. Furthermore, the graph shows that no information is available to indicate whether cylinders showing non-significant expansion (from 0.01 to 0.1 percent) at this time represent major-, minor-, or even nonexpansive rocks; one-half of the minor-expansion rocks would not show any length increase, thus behaving similarly to most of the nonexpansive rocks.

On the other hand, it appears that all cylinders showing a length increase above 0.1 percent after 5 wk of testing should be classified in the early-major-expansion group and cylinders showing a slight expansion (from 0.04 to 0.1 percent) at this time most probably belong to the minor-expansion group; but cylinders with a smaller expansion might be minor-expansion or nonexpansive rocks, because one-quarter of the 109 nonexpansive cylinders show a slight expansion (between 0.01 and 0.05 percent) not only at 2 but also at 5 wk. It is very difficult to establish by short-term tests which samples belong to the minor-expansion group, because of the variable-expansion behavior of this group at early test ages.

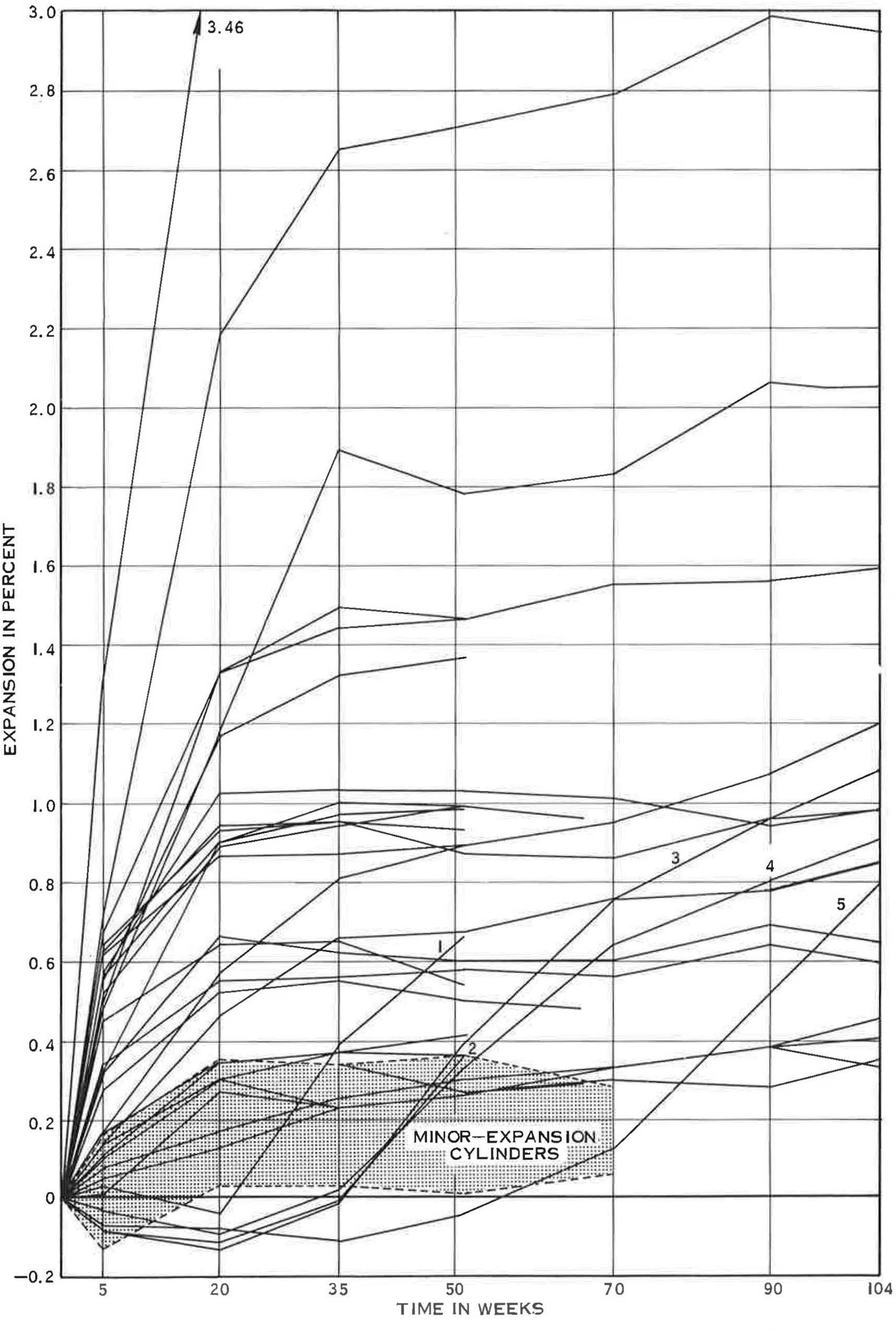

Figure 5. Expansion vs time for rock cylinders in NaOH; curves 1, 2, 3, 4 and 5 of late-major-expansion cylinders; other curves, early-major-expansion cylinders.

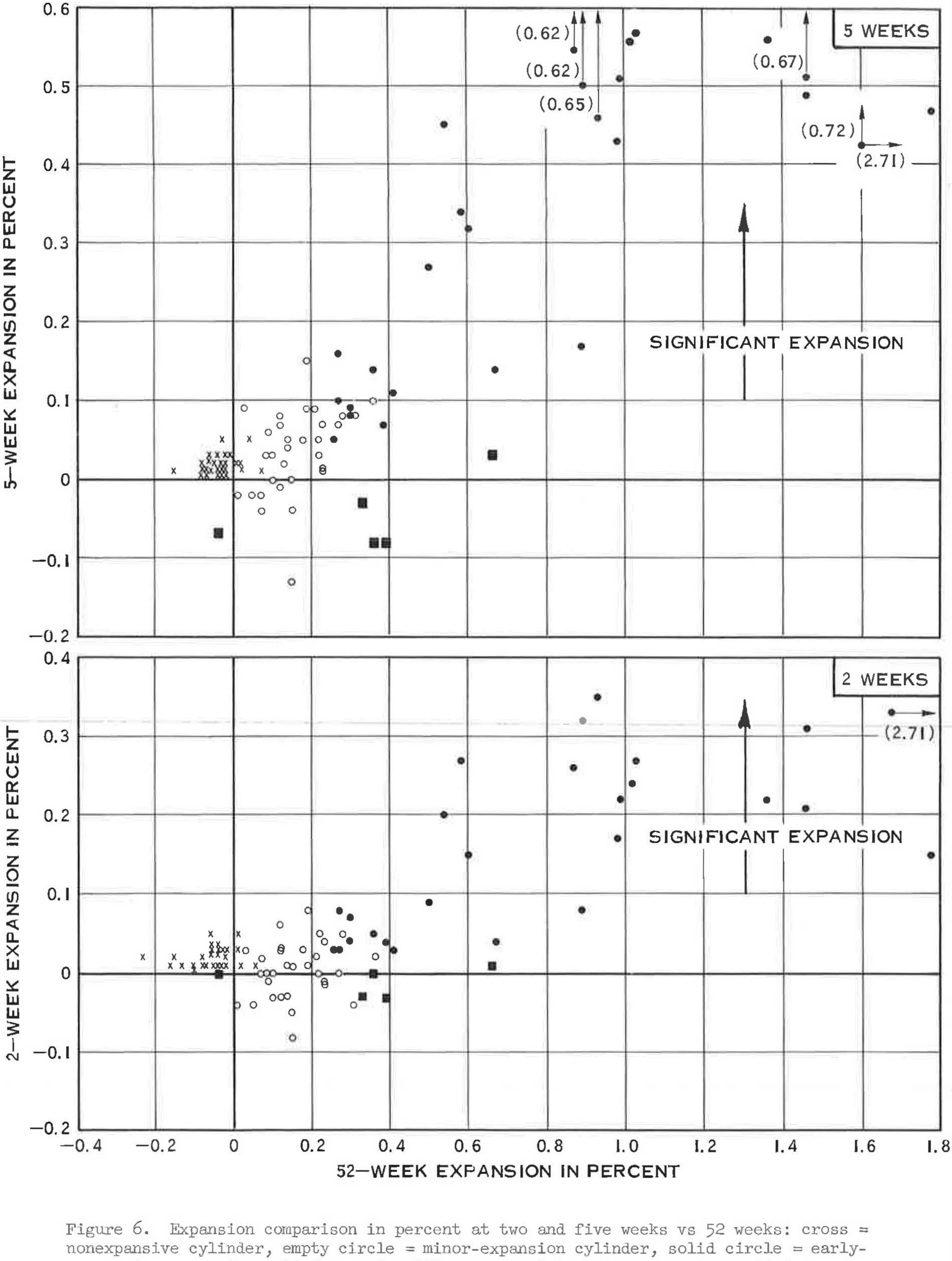

Figure 6. Expansion comparison in percent at two and five weeks vs 52 weeks: cross = nonexpansive cylinder, empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, and solid square = late-major-expansion cylinder.

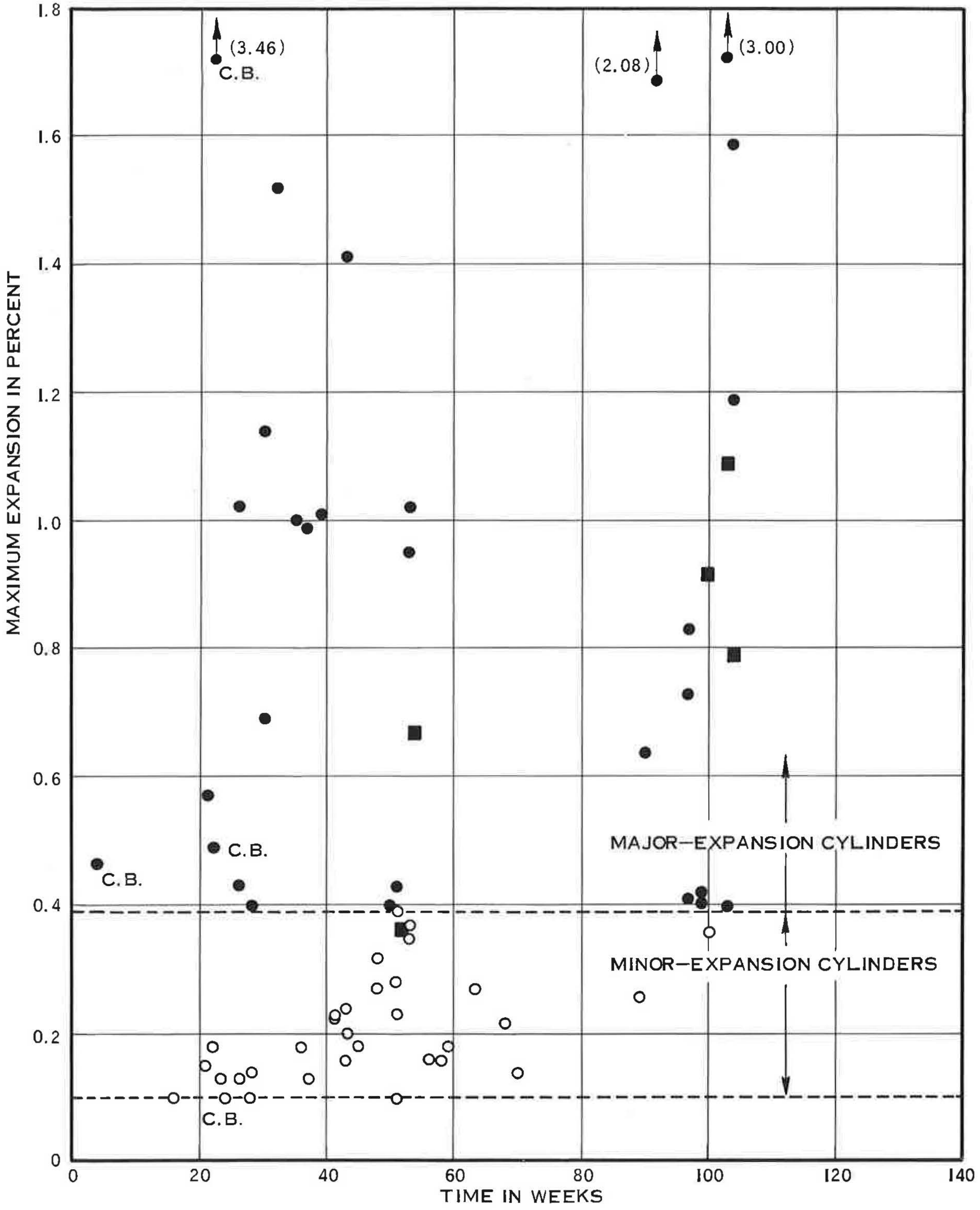

Figure 7. Test duration vs maximum expansion: empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.

Maximum Expansion

The maximum expansion registered in the set tested for 1 to 2 yr was 3. 5 percent. Figure 7 illustrates the great differences in the time taken for maximum expansion of various cylinders to occur. It also demonstrates the difference between the minor- and both major-expansion groups. When considering these data, however, it should be kept in mind that the tests are not yet completed and some cylinders will eventually show an even higher maximum length because the expansion may be continuing at a very slow rate. This applies especially to the samples that have been under test for only 1 yr.

PETROGRAPHIC CHARACTERISTICS OF EXPANDING GULL RIVER ROCKS

No single feature of composition or texture has been found to be connected with the expansion behavior of the Gull River rocks. Detailed examination of the expansive rocks showed certain megascopically noticeable heterogeneities such as differences in color, grain size, density, dolomite content, and presence of clay seams, quartz grains and fossils. This may apply not only to samples taken from different members of the same geological unit but also to different layers of the same geological member and even parts within a layer. On the other hand, rocks having a seemingly identical petrographic appearance might differ considerably in their expansion characteristics as shown in the Appendix by the differences in the responses of cylinder pairs to NaOH. These facts prevent prediction, on the basis of characteristics revealed by normal petrographic techniques, of whether a rock is expansive or not and to which expansion group it might belong.

Composition of Expanding Rocks

Percentage of Dolomite in Carbonate Portion. —The dolomite to calcite ratios of the rocks were determined in two ways, by X-ray analyses and by determining the calcium and magnesium contents by wet chemical analyses, and then calculating the ratio assuming that all of the magnesium was present as dolomite and the excess calcium was present as calcite. The results obtained by the two different methods do not differ significantly.

The relationship between the percentage of dolomite in the carbonate portion of expansive rocks and the maximum expansion in percent is shown for 55 rocks in Figure 8. (Five points showing the maximum shrinkage of nonexpansive cylinders are included in the graph.) The graph shows that although there is no absolute relationship between expansion and dolomite content, most of the expansive rocks contain less than 40 percent dolomite and rocks containing less than 12 percent dolomite are usually not highly expansive.

Both the minor- and early-major-expansion groups have a wide range of dolomite contents from 4 to 78 percent and from 4 to 60 percent, respectively. Both groups therefore include limestones, dolomitic limestones and calcitic dolomites. However, almost two-thirds of the early-major-expansion group contained from 10 to 30 percent dolomite in the carbonate fraction and would therefore be classed as dolomitic limestones. Three of the early-major-expansion limestones contained less than 8 percent dolomite in the carbonate portion, making little dolomite available for dedolomitization, which is a part of the alkali-carbonate reactivity (8).

The five late-expansion cylinders are all calcitic dolomites with the very small variation in dolomite of 78 to 85 percent. This range might increase when more cylinders of this type are available for testing.

Percent Acid-Insoluble Residue. —The relationship between the amount of acid-insoluble residue found in the alkali-reactive carbonate rocks and the maximum expansion in percent for all cylinders is shown in Figure 9. The data indicate that all cylinders having maximum expansion of more than 0. 5 percent fall within the range of 8 to 30 percent of insoluble residue and are therefore classified as impure carbonate rocks. Four of the early-major-expansion cylinders contained 20 to 30 percent of in-

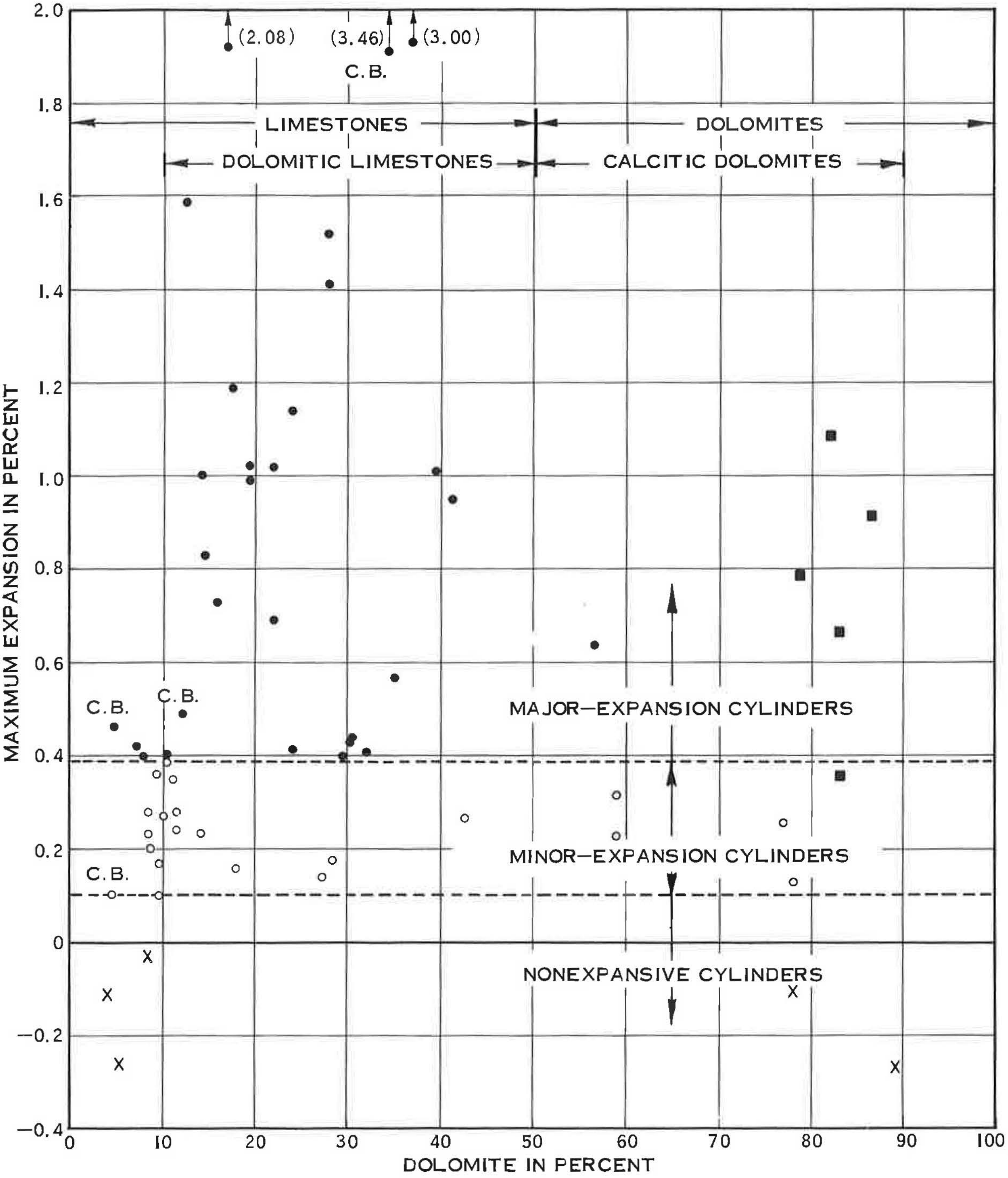

Figure 8. Dolomite in percent of carbonate portion vs maximum expansion: cross = nonexpansive cylinder, empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.

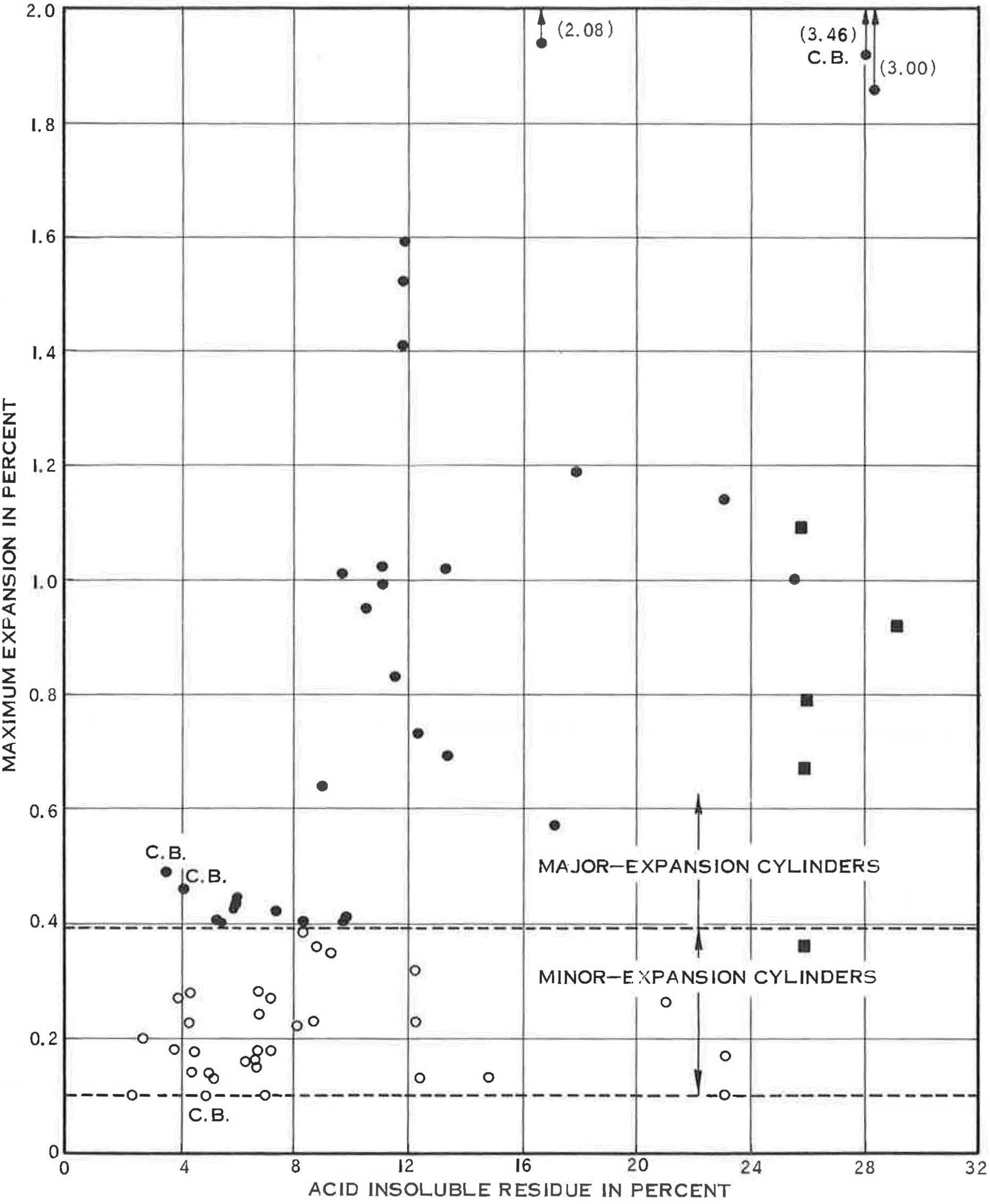

Figure 9. Acid-insoluble residue vs maximum expansion: empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.

soluble residue and all five late-major-expansion cylinders were characterized by the very narrow range of 25 to 30 percent of noncarbonate constituents; thus one-quarter of the major-expansion groups had 20 to 30 percent of insoluble residue. Although the minor-expansion group covered a range from 2 to 24 percent of insoluble residues, most of the samples belonged to pure or relatively pure carbonate rock varieties.

No sample of Gull River rocks which contained more than 30 percent of residue showed expansion. At the other end of the scale, one sample with less than 5 percent dolomite, which showed rapid initial length increase but broke after 4 wk of testing, had only 4 percent of impurities and therefore represented a pure limestone (see Appendix—"Cracking").

Noncarbonate Constituents.—The X-ray analyses of the acid insoluble residues, performed by R. Laakso on 40 expanding samples, showed that all expanding rock groups contained illite, chlorite and quartz. Illite usually was the most abundant, but in a few samples, quartz was the most abundant, noncarbonate mineral. (It may be significant that the 10Å illite peak on the diffractometer trace was asymmetrical toward low angles in most samples. On heating, a sharper, more intense and symmetrical peak resulted. The asymmetry is probably due to significant hydration of illite (R. Laakso).) In each sample illite was present in larger amounts than chlorite. Potash feldspar was, in general, more abundant than plagioclase, but both feldspar types were usually present in very small amounts. The amounts of clay minerals and/or clastic grains are, of course, reflected in the amounts of insoluble residues, but they do not seem to be related to either the amount of dolomite or the degree of expansion.

Some of the expanding samples contained an expanding type of clay mineral. It is, however, unlikely that this mineral is responsible for the expansive properties of the rocks because it is present in very small amounts and no relationship could be established between its presence and the degree of expansion. Furthermore, this mineral was more frequently absent than present in the early-major-expansion group.

The late-major-expansion group with a relatively high noncarbonate content showed greater uniformity in noncarbonate mineral composition than the other groups. It was characterized by approximately the same amounts (medium to high) of illite and quartz, medium amounts of chlorite, and very small amounts of feldspars and of an expanding clay mineral.

These findings are similar to those reported by Gillott for rocks from the two Kingston quarries. No direct relationship was found between reactivity and composition (3, p. 771).

Texture

A fine-grained and relatively uniform texture is reported to be one of the deciding factors in determining whether a rock is alkali reactive or not. As described and illustrated in photomicrographs by Gillott (3) and Newlon and Sherwood (7), the expansive rocks are partially dolomitized calcilutite containing isolated dolomitic rhombs in a matrix of microcrystalline calcite and clay. This feature also appertained, in general, to highly expansive rocks of the Gull River formation belonging to the early-major-expansion group, but detailed examination of the numerous expansive rocks showed that their texture is quite heterogeneous on the thin section scale. The dolomitic rhombohedrons vary in size in different specimens and frequently in the same specimen. In the latter case, the presence of two generations of dolomitic rhombohedrons is indicated. The dolomite may occur more or less evenly distributed, or in patches or lenses, or it may be more concentrated in layers which may also be richer in clay minerals and/or clastic quartz grains. In some instances the concentration is so narrow and well defined that it may be referred to as a dolomitic clayey stylolite along which the cylinders are apt to break during NaOH immersion, as described in the Appendix.

The occurrence of fine clayey trains varying in size and concentration is typical for most of the major-expansion cylinders (Fig. 10). These stylolites, practically devoid of dolomite, may represent the formerly evenly distributed clayey and organic material that concentrated during dolomitization of the rock. They are, however,

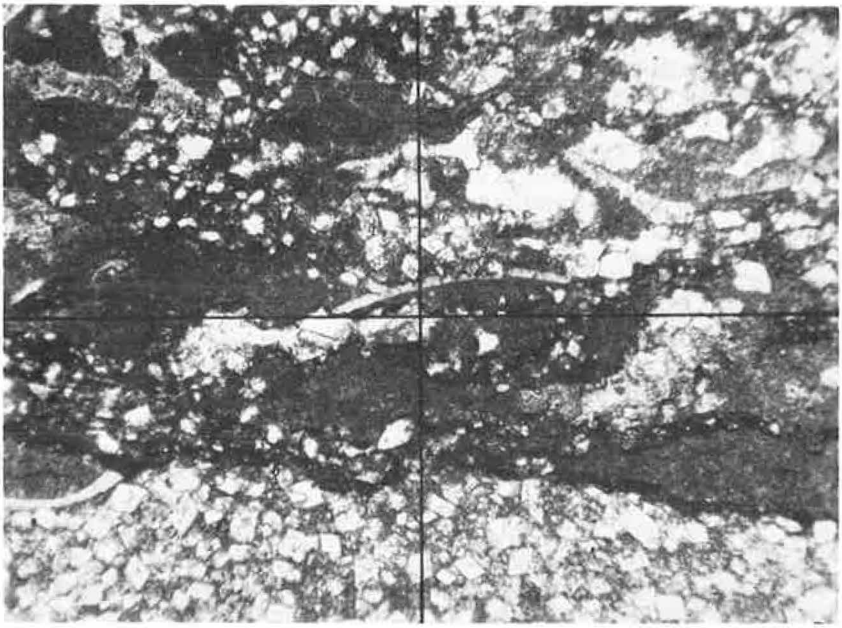

Figure 10. Argillaceous dolomitic limestone of early-major-expansion type. Black argillaceous stylolites border dolomite-rich areas (180X).

usually not so pronounced as to prevent the preparation of cylinders perpendicular to the direction in which they extend and to the general sedimentation layering. It might be expected that these clayey concentrations open the texture of the rock in a direction perpendicular to their main expansion and thereby contribute to the expansion of the rocks in concrete. This would explain why cylinders and prisms cut parallel to the layering show a lower degree of expansion in the direction of their longitudinal axis (Table 1, Sample 1728 in the Appendix). Although gradations in the texture from a very fine-grained uniform lithographic variety to heterogeneous, fossiliferous and/or pseudo-oolitic varieties are noticeable, a simple relationship does not seem to occur between the textural particularities described and the degree of expansion.

The texture of the late-major-expansion rocks, which are classified petrographically as silty-argillaceous calcitic dolomites (Fig. 11), closely resembles that developed in areas of dolomite and clay concentrations visible in thin sections of the early-major-expansion group (see Figs. 10 and 12—Appendix). It is similar to the texture described in detail by Gillott (3) for the slightly reactive rock occurring in the 24- to 30-ft section of the Kingston quarry. In the late-expansion group very finely crystalline euhedral dolomite aggregate contains larger dolomite rhombohedrons (about 0.1 mm in size) as well as evenly disseminated coarse-sized silt grains of quartz (about 0.05 mm in diameter) and scarce rounded quartz grains in medium sand size (0.5 mm). The matrix between these minerals is formed by argillaceous material and very fine-grained calcite. The latter may occur also in the form of larger-grained patches containing small dolomite euhedra. For one late-expansion sample, the amount of quartz grains was distinctly lower and that of the argillaceous matrix correspondingly higher in comparison with another sample that had the same percentage of insoluble residue.

Future Work

The work is proceeding by testing additional samples in order to correlate the expansion of the small cylinders with that of large specimens equal in volume to Swenson and Gillott's prisms (8).

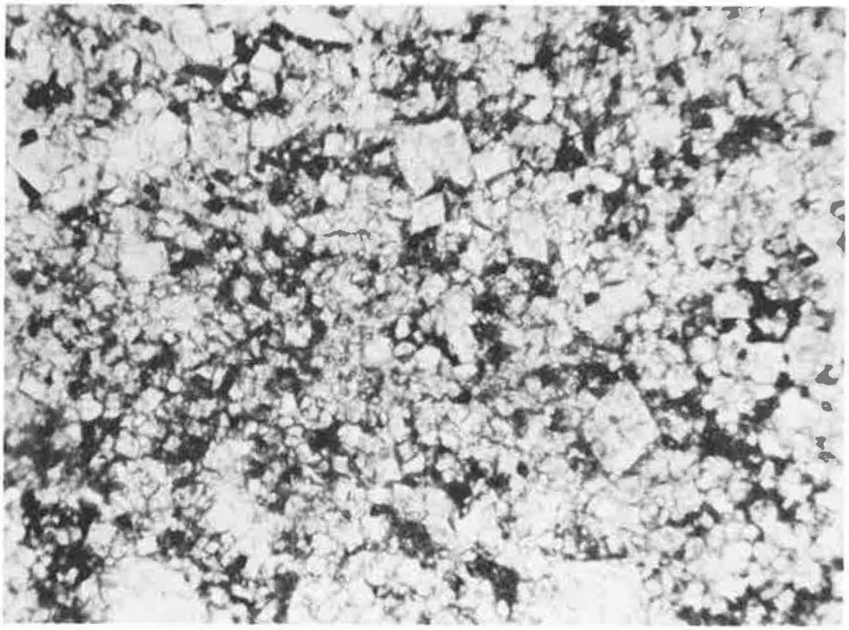

Figure 11. Argillaceous calcitic dolomite of late-major-expansion type (180X).

In an attempt to correlate the expansion of concrete made of expanding Gull River aggregate with the expansion of the small cylinders in NaOH, large block samples of the carbonate rocks were obtained. After small test cylinders from along the whole cross-sections of the blocks are prepared, the material will be crushed and used as aggregate in concrete specimens.

SUMMARY

The carbonate rocks from the Gull River formation, suspected of being alkali reactive, were tested in NaOH solution in the form of small cylinders. Samples showing more than 0.1 percent of expansion were classified as expanding rocks and divided into three groups based on the amount and time of the maximum expansion observed: the minor-expansion group with less than 0.40 percent expansion, the early-major- and the late-major-expansion groups with at least 0.40 percent expansion. The maximum expansion found in the samples tests for 1 to 2 yr was 3.5 percent, but in a cylinder on which the test was recently begun, expansion has reached 4.4 percent in 26 wk.

The early-major-expansion group which usually showed distinct expansion in the first 2 to 5 wk consisted of dolomitic limestones, some calcitic dolomites and a few limestones proper. Inasmuch as this group contains rocks with from 3 to 30 percent of acid-insoluble residues, carbonate rock varieties ranging from pure to distinctly argillaceous and occasionally quartzose silty varieties were present.

Distinctly expanding calcitic dolomites, which started to expand after at least 25 wk of NaOH immersion, were contained in the late-major-expansion group. This group was much less abundant than the other two and its petrographic characteristics were much more uniform. It was characterized by more than 75 percent of dolomite and by 25 to 30 percent of noncarbonates. The late-major-expansion cylinders continue to expand after 2-yr immersion in NaOH and expansion measurements are still being made on this group of samples. The maximum expansion at the last reading was more than 1 percent. Any material in this class might be suspected of causing alkali-aggregate reaction in concrete made with high alkali cement and exposed to humid conditions. Detection of the late-expansion group is somewhat simplified because, assuming relatively complete sampling, the data indicate that material in this group always occurs at locations in which material showing early-expansion of minor or major proportions is also present. Thus, in the cases investigated, the existence of a problem requiring corrective action would have been detected by early expansion results. However, the existence of the late-expansion group eliminates the possibility of early detection of the expansion characteristics of individual layers, which in some cases may be necessary if selective quarrying operations were to be considered in an attempt to avoid the problem.

The minor-expansion group comprised about one-half of the expanding cylinders. Rocks having this characteristic were found in all locations where the major-expansion layers occurred and also in a few quarries in which the latter were not detected. Petrographically, the minor-expansion group was rather heterogeneous and covered approximately the same range of petrographic properties as the major-expansion rocks. It has to be emphasized that not all cylinders showing little or no expansion in the first 2 or even 5 wk belong to this group, because such cylinders may later expand and be classified in the major-expansion group; or they may even decrease in length and may not be really alkali reactive. The significance of this group as far as volume changes in concrete are concerned has not been established, but such rocks may add to the expansion of concrete when included with highly expanding rock varieties.

No principal difference in the type of noncarbonate minerals was noticeable in the three expansive groups. Although the clay minerals were usually the most abundant constituents, quartz may be a relatively abundant constituent especially in the late-expansion group.

The texture of the expansive carbonate rocks varied from lithographic with dolomitic and argillaceous stylolites developed in limestones to microcrystalline in dolomites.

Expanding carbonate rocks from the Gull River formation are concentrated in the Kingston area (six locations) but also occur in two locations outside of this area.

ACKNOWLEDGMENTS

Permission to publish the data on the expansive Gull River carbonate rocks was granted by The Hydro-Electric Power Commission of Ontario. The author wishes to thank and to acknowledge gratefully the generosity of D. Moddle, chief of the Laboratory Branch of the Department of Mines of Ontario and Mr. R. Laakso for the performance of X-ray examination. Finally, she wishes to acknowledge the assistance of her associates, in particular that of T. G. Clendenning, Masonry Research Engineer, for his continued interest and support and of D. Harrison of the Chemical Research Department for supplying numerous chemical data.

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Appendix

Detailed Observations on Cylinders

Cracking. —Cracking and chipping of the test cylinders are relatively common phenomena, especially in the early-expansion group. However, only four cylinders, three of them belonging to the early-major-expansion group, broke at an early testing age. In this regard one cylinder was interesting because it showed the effect of a clayey-dolomitic seam or stylolite (1.0 mm in thickness) occurring in a pure lithographic limestone (calcilutite, Fig. 12). The rock contained 4.1 percent dolomite and 4.7 percent insoluble residue. The cylinder expanded almost one-half percent in 4 wk, then the top cone, 0 to 2 mm in thickness, broke off along the slightly inclined stylolite. The somewhat shortened cylinder (1.0976 in. in length), with a reworked cone, consisted practically of pure limestone only and did not expand during the subsequent 40-wk immersion in NaOH.

The location and type of cracking appear to be correlated with some textural features of the rock as shown above. But neither the number of cracks nor their depth is directly related to the intensity of expansion or to the amount of noncarbonate impurities, as shown in Figure 13 by cylinders photographed after different periods of immersion. Whereas cylinder A (1728) with the greater expansion showed a hardly noticeable crack, cylinder B (1729), which expanded considerably less, developed numerous cracks which continued to increase in length and depth. The directions of the cracks were influenced to a great extent by the seemingly brecciated texture of the rock and the presence of stylolitic seams as shown by the thin section made of this sample and illustrated in Figure 10. Both cylinders reached almost the maximum expansion at the time the last photograph was taken.

The last cylinder, C, (Fig. 13) had a length increase of 3.6 percent after 7 wk of immersion. The cylinder is bent and shows an irregular pattern cracking. This cylinder, consisting of a greenish dolomitic limestone (11.5 percent insoluble residue),

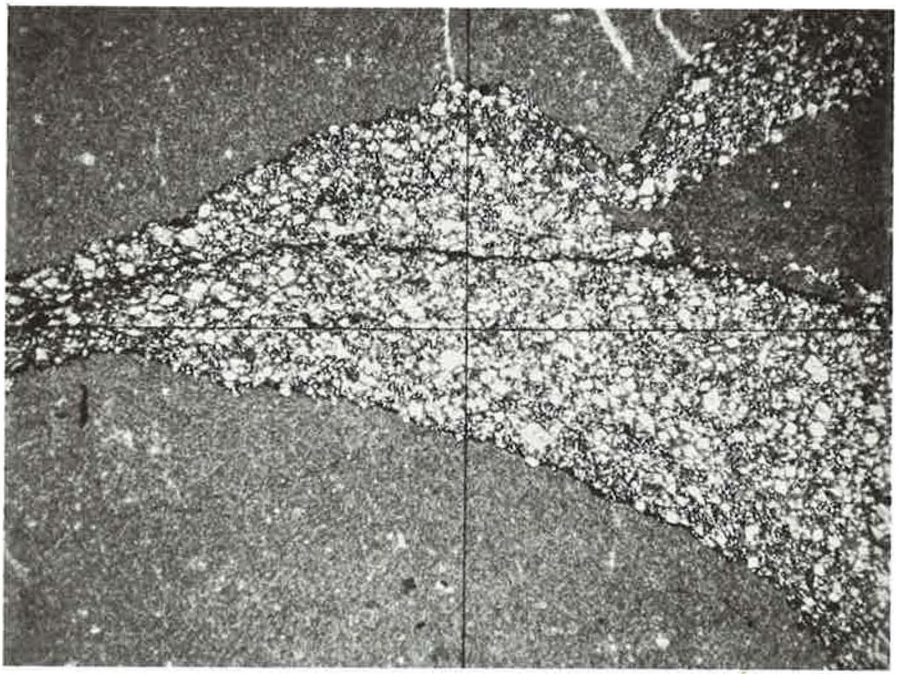

Figure 12. Pure lithographic limestone with dolomite-clay stylolitic concentrations; early-expansion type (39X).

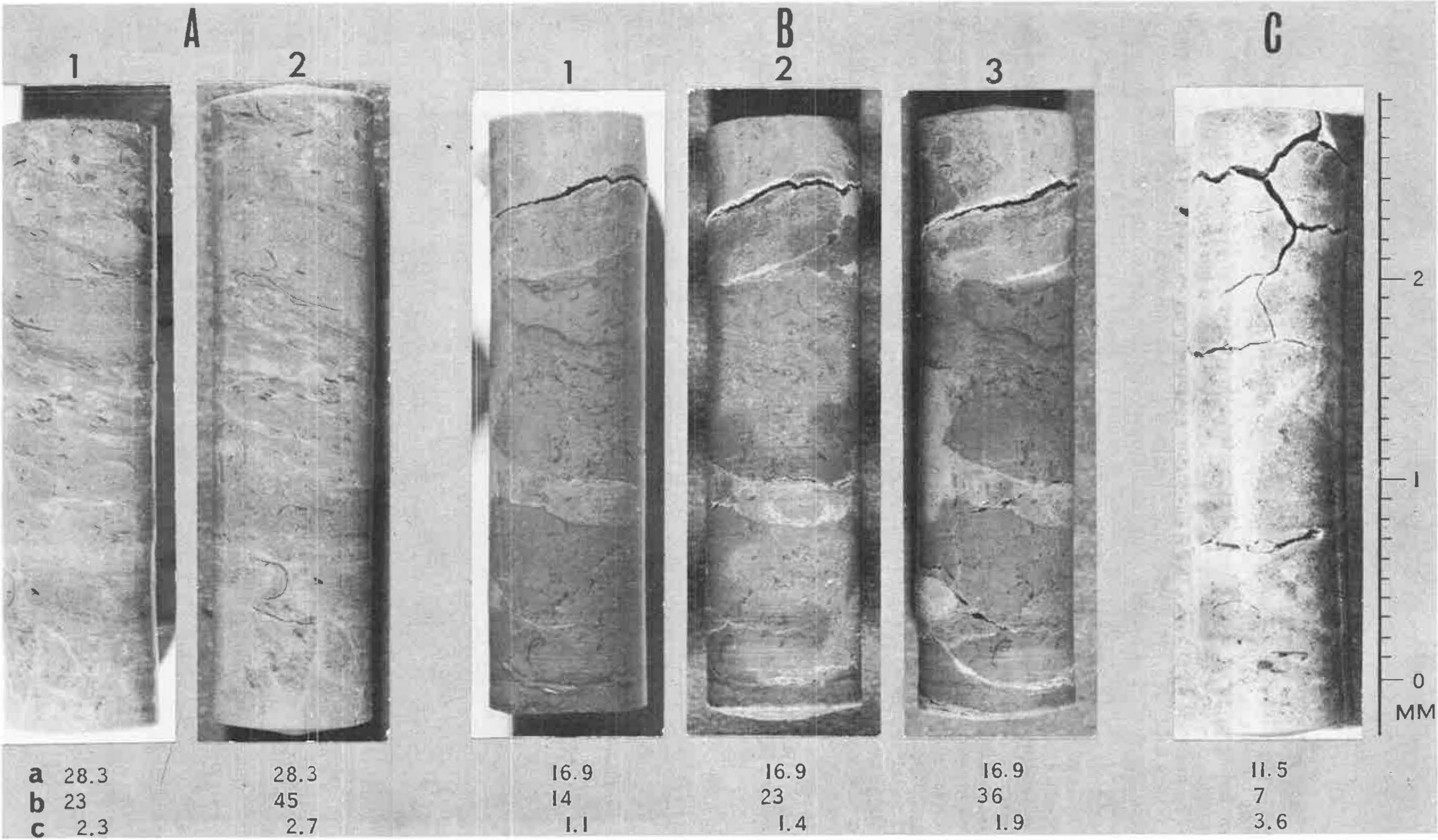

Figure 13. Cracks in expanding cylinders: (a) insoluble residue, in percent; (b) time of NaOH immersion, in weeks; (c) expansion, in percent.

did not break although it expanded 4.4 percent in 26 wk, the highest expansion value obtained to date on Gull River rocks.

Pairs of Cylinders.—Pairs of cylinders from the same sample usually gave similar expansion values within the limits of measurement error. In the minor-expansion group one of a pair of cylinders might not reach the lower limit of significant expansion (0.1 percent) and such cylinders therefore would be considered nonexpansive. The maximum expansion values of four major-expansion pairs with larger than usual differences within the pairs are given in Table 1. They demonstrate the heterogeneity of the samples that seemed megascopically rather uniform.

TABLE 1

DIFFERENCES IN MAXIMUM EXPANSION OF CYLINDER PAIRS

Sample	Maximum Expansion (%)			Diff. of Larger Value (%)
	Cyl. 1	Cyl. 2	Diff.	
1728	1.19[1]	2.08[2]	0.89	43
1729	3.00[2]	3.46[2]	0.46	13
1874	0.36[2]	0.67[2]	0.31	46
1882	0.69[1]	1.02[1]	0.33	32

[1] Cylinder drilled parallel to layering.

[2] Cylinder drilled at right angle to rock layering.

The difference in the expansions of cylinders cut parallel and perpendicular to sedimentation layering, is already well known (8) but may be normally much less than shown in the first pair (1728). The difference in the maximum expansion of the second pair (1729) might have been much greater if the more strongly expanding cylinder had not broken after 19 wk of immersion. The third pair (1874) represents a late-expansion rock (Curves 1 and 2, Fig. 5) and shows the slower rate of expansion in one cylinder in comparison with the second. The fourth pair (1882) belongs to the early-expansion group, as do the first two pairs. Because both cylinders were cut parallel to the layering, the maximum expansion of the rock might be greater than registered by these two cylinders.

Alkali-Reactive Carbonate Rocks in Indiana—A Pilot Regional Investigation

DAVID W. HADLEY, Research Geologist, Applied Research Section, Portland Cement Association

A study of carbonate rocks exposed in Indiana indicated that by utilizing standard geologic field techniques coupled with specially developed simple, rapid laboratory tests, the distribution of the reactive rocks within the vertical sequence of beds and the geographic areas in which these reactive rocks were exposed could be rapidly delineated.

The reactive rocks are widely distributed in Indiana, with highly reactive material present in at least five of the formations exposed. Rock from at least one of these horizons is considered to have caused the disruption of field concrete. Fortunately, however, the reactive beds are normally thin, the general level of reactivity is low, and most of the highly reactive materials are of poor physical quality and consequently are not used frequently as concrete aggregate.

Studies on laboratory concretes show that many of the marginally reactive materials could be safely used as concrete aggregate if adequate precautions were taken.

•OBSERVED EFFECTS in concrete containing certain carbonate rocks as aggregate may involve at least two distinct types of chemical reactivity. One type, first reported by Swenson (1), involves disruptive expansion of the coarse aggregate particles; the other, described by Bisque and Lemish (2), is characterized by the development of siliceous reaction rims on the aggregate particles. The work of Bisque and Lemish (3, 4) on the rim-developing rocks, and that of Swenson and Gillott (5) and Hadley (6) on the expansive rocks, has shed additional light on the mechanisms of reactivity. Very little is known about the occurrence, relative abundance, and distribution of reactive rocks, information which is of immediate interest to the practicing engineer. As a first step in assembling such information, the Portland Cement Association Laboratories included in its research on reactive carbonate rocks a pilot field and laboratory investigation of the rocks exposed in a specific geographic area. Indiana was chosen for study because of its proximity, thick section of carbonate rocks exposed, and the presence of carbonate rocks with poor service records as concrete aggregates.

The investigation was designed to collect information on the occurrence and distribution of reactive rocks in the study area, and to develop and evaluate sampling and testing methods applicable to rocks exposed in other areas.

Preliminary laboratory work included the development of simple, rapid tests for both types of reactivity in rock samples. Therefore, the pilot study began with an integrated program of field sampling and laboratory testing to determine the geological and geographical distribution of both types of reactive rocks. Selected rocks of known reactivity were then collected in larger quantities and used as coarse aggregate in laboratory concrete tests to establish correlations between the preliminary laboratory test

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results and the properties of concretes containing these rocks. Additional testing of concretes made with the reactive rocks was performed to evaluate possible remedial measures.

Previous Studies

In 1945 Woods, Sweet and Shelburne (7) found that the expansion of concrete pavements in Indiana, which had led to map cracking and eventual blowups, could in many cases be correlated with the source of the coarse aggregate. In subsequent detailed investigations of rocks from these sources, Slate (8) found no evidence of alkali-silica reactivity, but Sweet (9) found that many of these rocks performed poorly in freezing and thawing tests of concretes. Patton (10) reported that many of the poorly performing aggregates were quite similar in lithology, and that rocks of this type were found primarily in limited zones of the Jeffersonville, St. Louis, and Kokomo formations. Patton felt that the poor service record of these rocks was probably due to poor durability under freezing and thawing conditions.

Types of Chemically Reactive Carbonate Rocks

Rim-Developing Rocks.—Bisque and Lemish (2) noted that certain carbonate rocks developed prominent reaction rims in concrete. These rims are composed in part of siliceous materials, first believed to have been derived from the cement paste. Subsequent studies (11) seem to indicate, however, that the rims are primarily the result of a redistribution of the siliceous components of the rock itself. The exact mechanism of rim formation is not yet clear nor has it been demonstrated that the development of rims per se indicates a deleterious chemical reaction.

Expanding Rocks.—The second type of reactive carbonate rocks expands rapidly both in concrete and in highly alkaline solutions. Hadley (6) found that the expansive rocks could be characterized on the basis of composition and texture. All were argillaceous dolomites or dolomitic limestones, and the most highly reactive of these rocks contained mixtures of calcite and dolomite and large amounts of clay. (Clay is used here as including all noncarbonate material in the rock having an equivalent spherical diameter of two microns or less. Clay contents were normally determined by subtracting from the total acid-insoluble residue the percentage of silt-sized and larger particles as estimated by petrographic techniques.) In addition, these rocks all shared a common texture, being composed of silt-sized dolomite rhombs "floating" in a matrix of clay and finely disseminated calcite. The expansion of these rocks accompanied the following chemical reaction between the alkali metal hydroxides and the mineral dolomite:

$$CaMg(CO_3)_2 + 2MOH \rightarrow M_2CO_3 + Mg(OH)_2 + CaCO_3$$

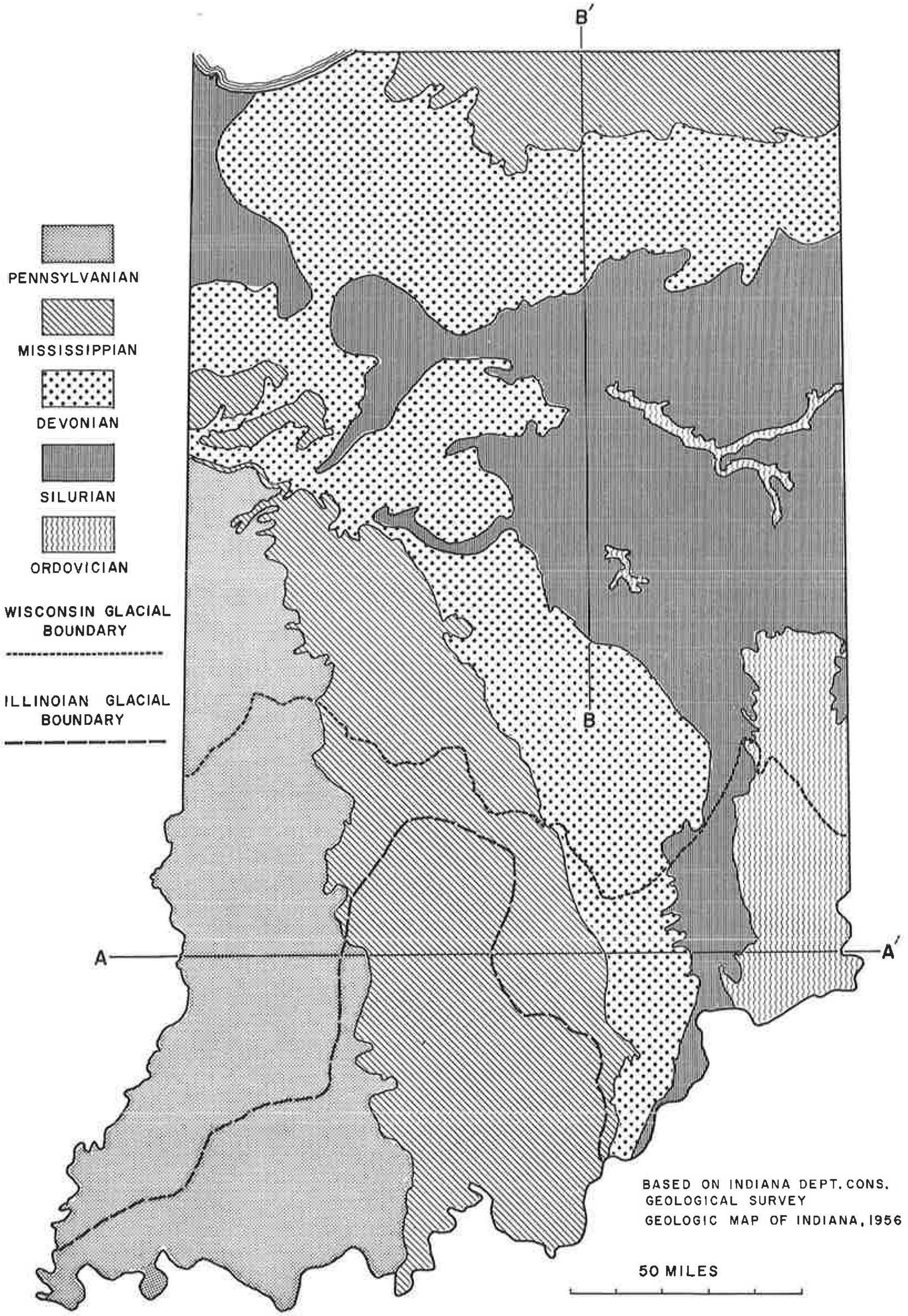
in which M = K, Na, or Li.

SAMPLING PROGRAM

Geologic Setting

The problems of locating reactive carbonate rocks in the field were much the same as would be encountered in the exploration for any mineral resource. Inasmuch as this phase of the study was essentially a geologic exploration, a summary of the pertinent features of the geology of Indiana has been included.

Structural Relationships.—Indiana lies in the central stable region of North America. In contrast to the highly contorted rocks found in those regions which have undergone periods of mountain building, deformation of rocks in the central stable region has been confined to mild warping and flexing. The resulting structural features are a series of broad domes and basins. The geologic map and cross-sections (Figs. 1, 2) show that Indiana lies between two of these basins. The rocks in northern Indiana dip gently northward into the Michigan basin, whereas in southern Indiana the dip is to the south-



BASED ON INDIANA DEPT. CONS.
GEOLOGICAL SURVEY
GEOLOGIC MAP OF INDIANA, 1956

Figure 1. Generalized geologic map of Indiana.

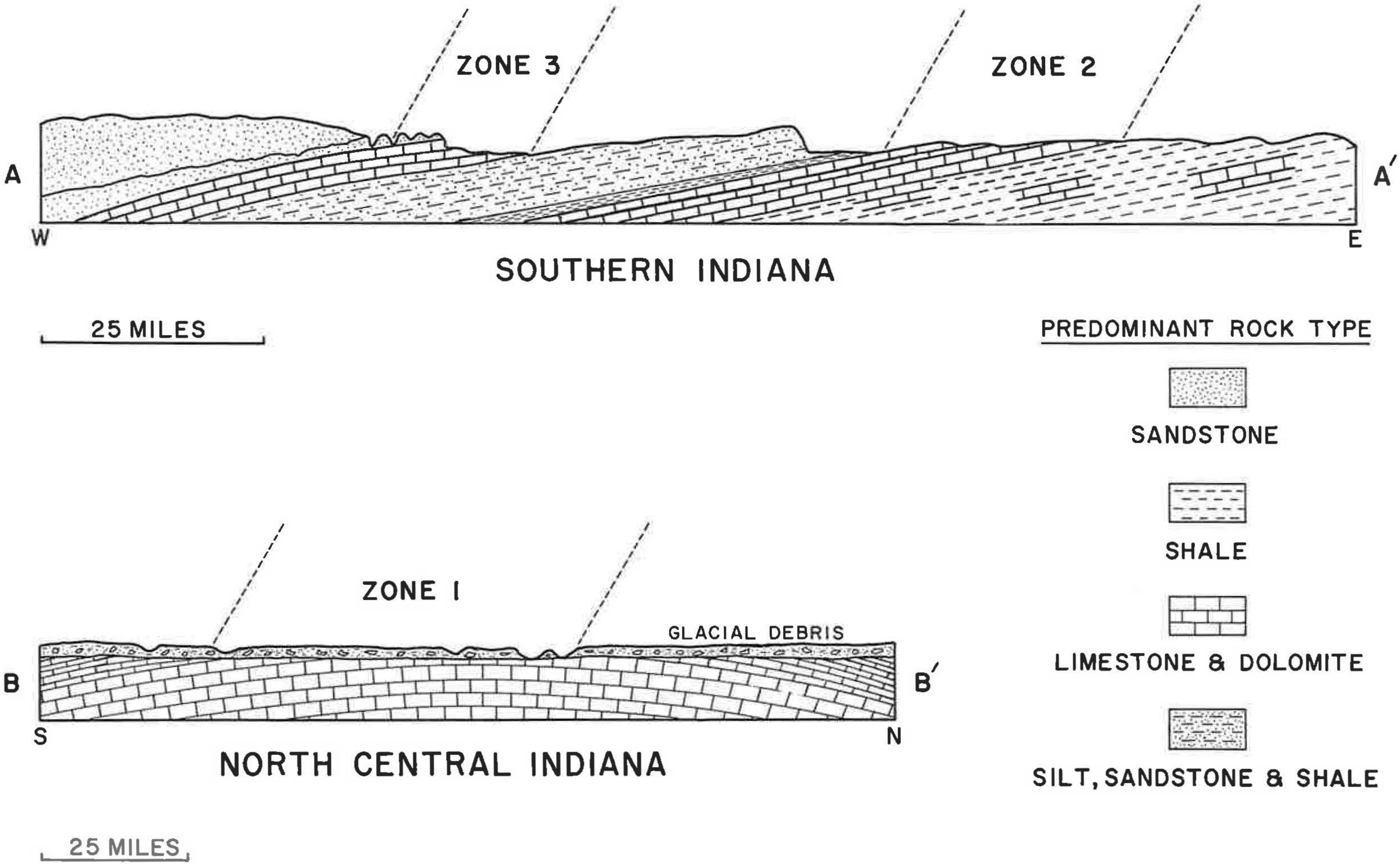


Figure 2. Diagrammatic cross-sections through southern and north-central Indiana showing major zones of limestone outcrop.

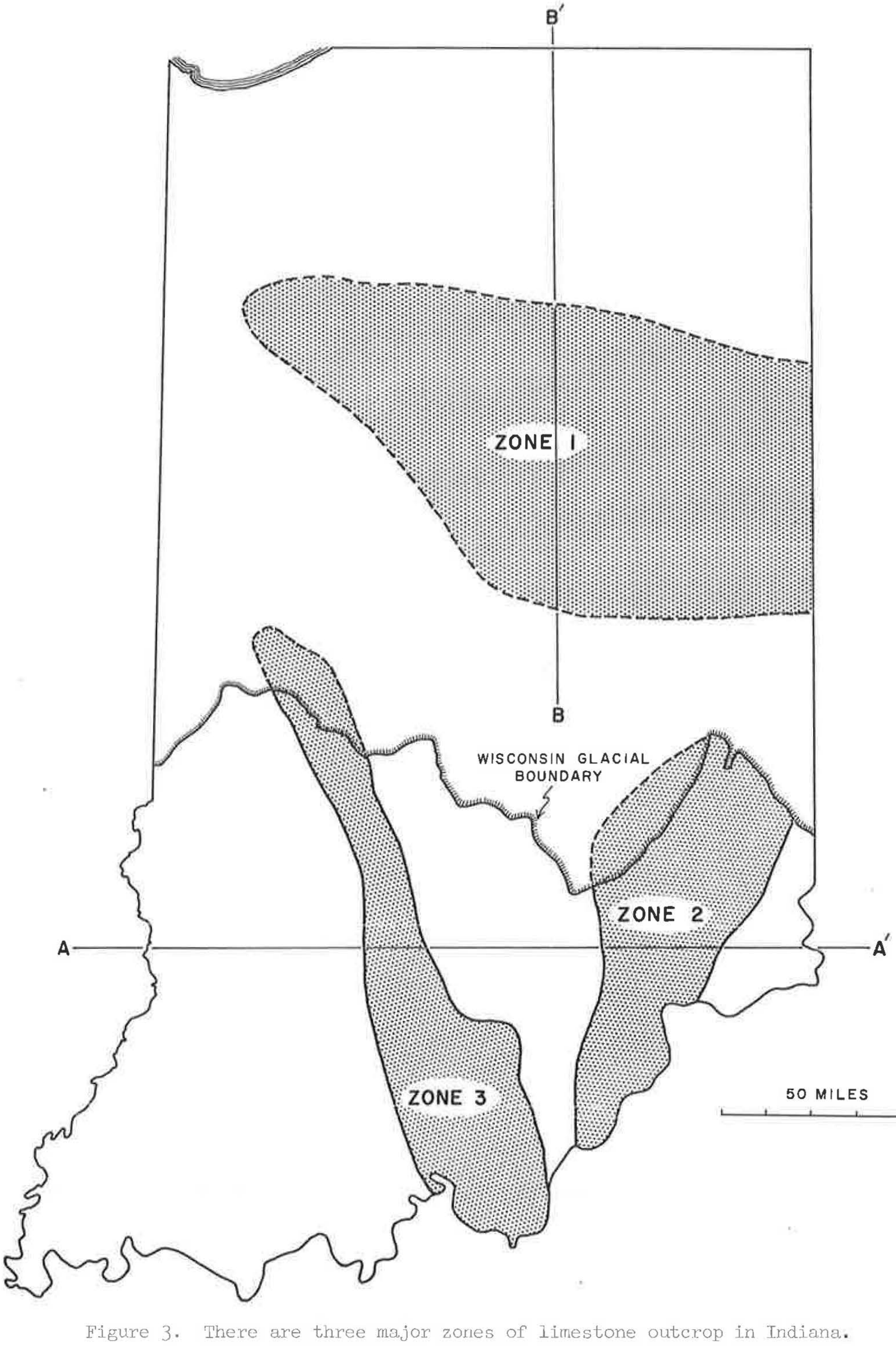


Figure 3. There are three major zones of limestone outcrop in Indiana.

west and into the Illinois basin. In north-central Indiana the strata pass through a transitional zone in which the rocks are essentially flat lying.

Glacial Deposits.—At least three times in the geologic history of Indiana much of the state was covered by the ice of the great continental glaciers. At the time of maximum advance the ice covered almost 85 percent of the state. Each time the ice retreated it left extensive deposits of glacial till.

These glacial deposits influence the location of crushed stone plants because quarrying is possible only in those glaciated areas where till is extremely thin or where erosion by the major streams or their tributaries has exposed the previously buried bedrock. The two principal till sheets exposed in Indiana are described in the following:

Illinoian Till.—More than half of southern Indiana is overlain by Illinoian till. The deposits are relatively thin, ranging up to only about 30 feet. Because this material

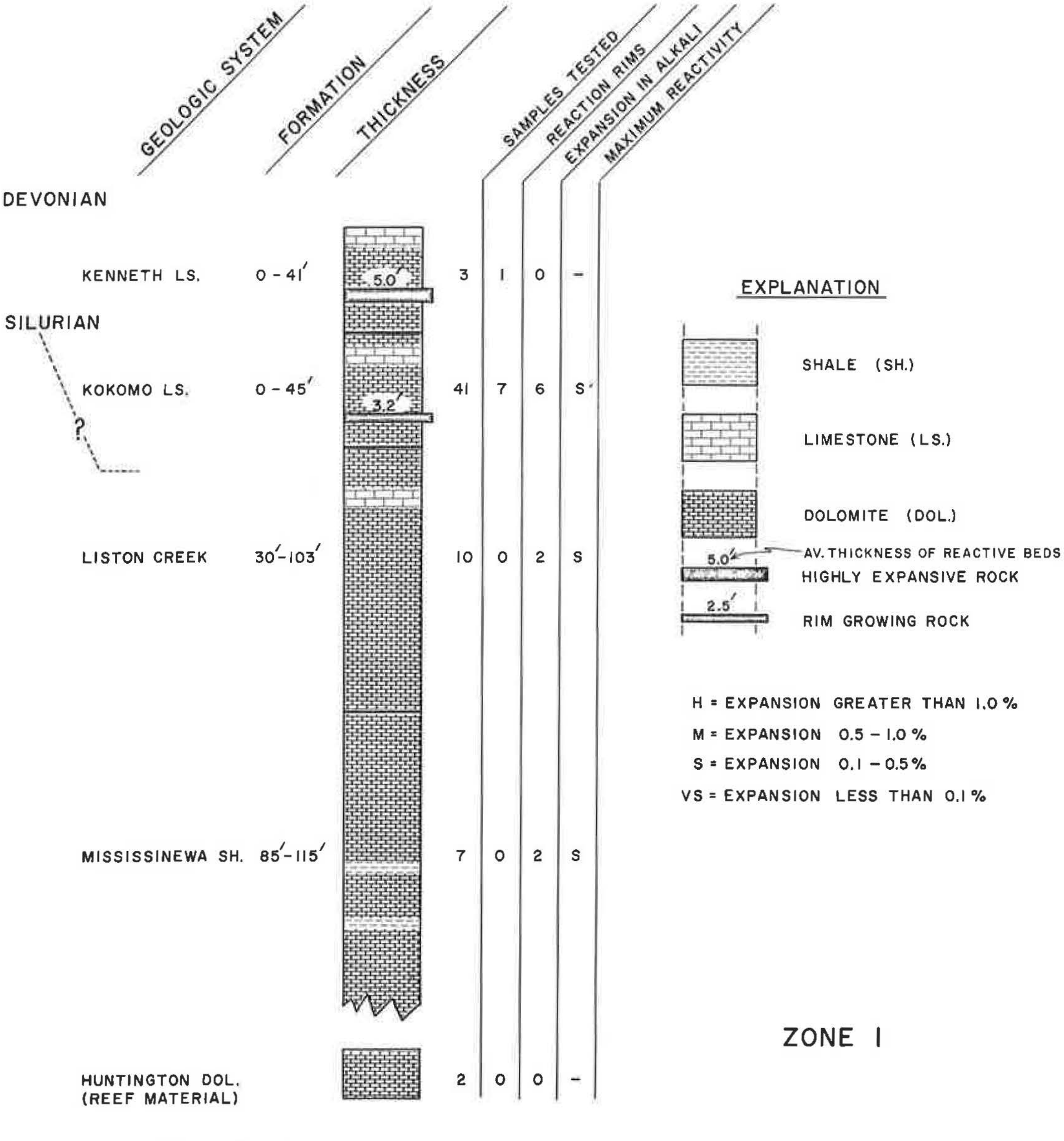
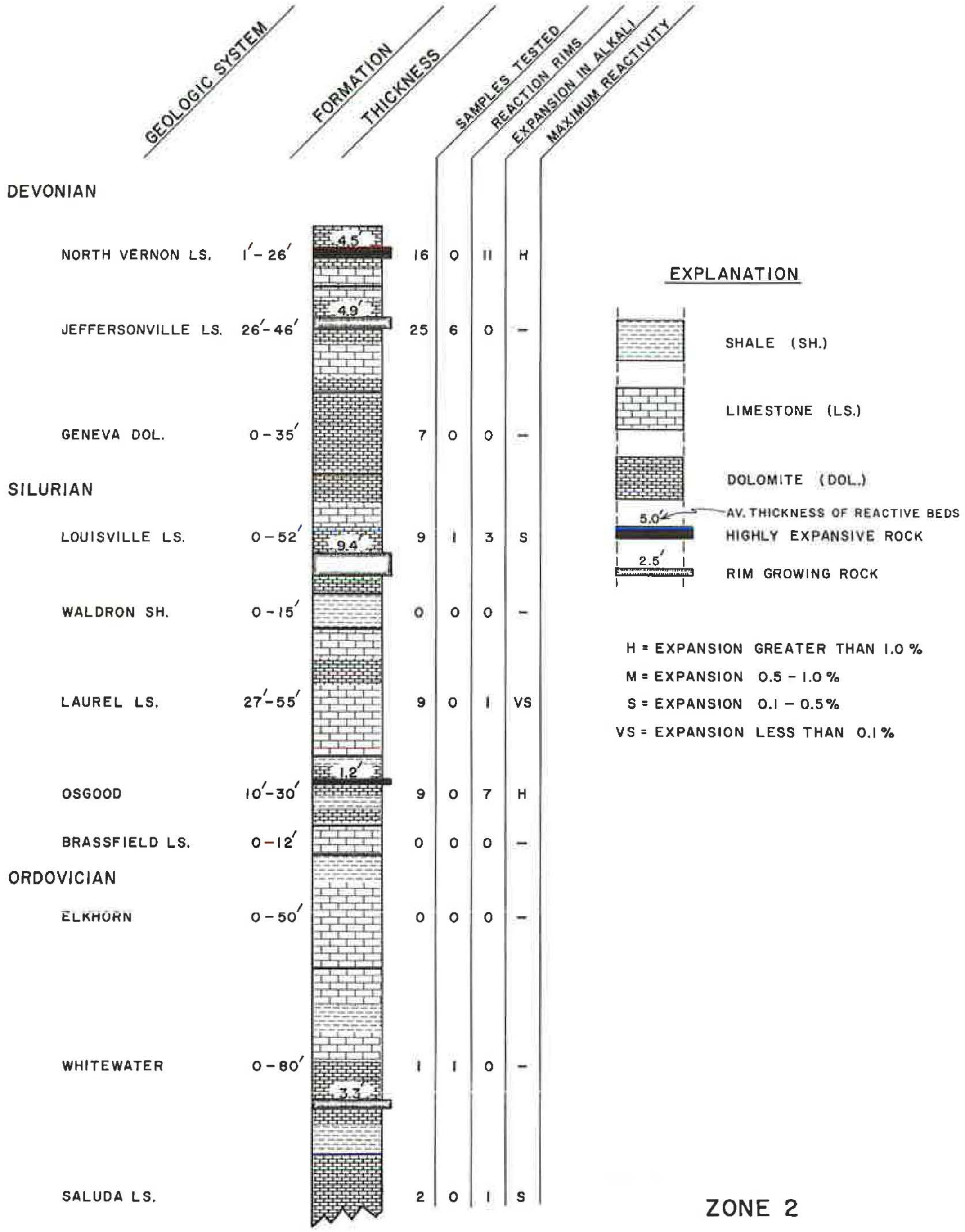


Figure 4. Columnar section showing distribution of reactive beds.



GEOLOGIC SYSTEM	FORMATION	THICKNESS	SAMPLES TESTED	REACTION RIMS	EXPANSION IN ALKALI	MAXIMUM REACTIVITY
DEVONIAN	NORTH VERNON LS.	1′ – 26′	16	0	11	H
	JEFFERSONVILLE LS.	26′ – 46′	25	6	0	–
	GENEVA DOL.	0 – 35′	7	0	0	–
SILURIAN	LOUISVILLE LS.	0 – 52′	9	1	3	S
	WALDRON SH.	0 – 15′	0	0	0	–
	LAUREL LS.	27′ – 55′	9	0	1	VS
	OSGOOD	10′ – 30′	9	0	7	H
	BRASSFIELD LS.	0 – 12′	0	0	0	–
ORDOVICIAN	ELKHORN	0 – 50′	0	0	0	–
	WHITEWATER	0 – 80′	1	1	0	–
	SALUDA LS.		2	0	1	S

Figure 5. Columnar section showing distribution of reactive beds.

C 227, could be used for a determination of the level of rock prism expansion below which the Indiana aggregates could be safely used with a given cement.

Strength Development in Concretes Made with the Rim-Developing Rocks

In studies of concretes made with a rim-developing Iowa carbonate coarse aggregate, Bisque and Lemish (4) found that under certain storage conditions the rate of strength development was adversely affected. Therefore, a series of tests was made to determine whether the rim-developing Indiana rocks would also affect the rate of strength gain.

Description of Concrete Mixes.—All mixes were maintained at a water-cement ratio of 0.40 and a slump of 1 to 2 in. The cement factor ranged from 6.3 to 6.7 sacks per cubic yard. Maximum aggregate size was ¾ in. and sand constituted 36 percent of the absolute volume of aggregate.

Materials.—The cement used was Cement 14 of the "Long-Time Study of Cement Performance in Concrete" (12). This cement, which is of high alkali content (0.06 percent Na_2O and 1.30 percent K_2O), is regularly used in tests of the alkali reactivity of aggregates at these laboratories. The fine aggregate was the Elgin, Illinois, sand described earlier; the coarse aggregate was either a rim-developing carbonate rock from a laminated zone of the Jeffersonville, Indiana, limestone or an inert gravel from Elgin, Illinois. The chemical analysis, specific gravity, and fineness of the cement, together with the grading, specific gravity, and absorption of the aggregates are given in Table 7.

Specimen Preparation.—Specimens were 3- by 6-in. cylinders cast in accordance with ASTM C 192-59.

Curing.—After casting, specimens were stored immediately under wet burlap covered with a polyethylene sheet. After 20 to 24 hr the specimens were removed from the molds and stored either at 100 F over water, at 73 F and 100 percent RH, or in a wetting and drying cycle of 2 days in water at 73 F followed by 5 days in air at 100 F and 24 percent RH.

Testing.—Cylinders were tested in compression at 7, 28, 90, and 180 days and at 1 yr.

TABLE 7

CHARACTERISTICS OF MATERIALS USED IN LABORATORY CONCRETE TESTS OF RIM-DEVELOPING COARSE AGGREGATE

Cement (LTS 14)		
Determination	Result	
	Value	Unit
SiO_2	22.1	%
Al_2O_3	4.7	%
Fe_2O_3	3.0	%
CaO	62.9	%
MgO	2.4	%
SO_3	1.7	%
Na_2O	0.06	%
K_2O	1.30	%
Tot. alk., as Na_2O	0.92	%
Mn_2O_3	0.13	%
Loss on ignition	0.9	%
Insol. residue	0.31	%
Sp. surface:		
Wagner	3434	sq cm/gm
Blaine	1880	sq cm/gm
Passing No. 325 sieve	97.7	%
Sp. gr.	3.183	-

Coarse Aggregates			Gradation (% ret.)		
Type	Bulk Sp. Gr.	Absorp.[a] (% by wt.)	¾ In.	⅜ In.	No. 4
Elgin, Ill., gravel	2.65	2.00	35	65	100
Jeffersonville crushed rock	2.49	6.31	35	65	100

[a] 24 hr.

TABLE 8

ADVERSE EFFECT OF RIM-DEVELOPING ROCKS ON STRENGTH DEVELOPMENT RATE IN CONCRETE[a]

Test Age (days)	Compressive Strength (psi)					
	Stored 100 F Over Water		Stored 73 F, 100% RH		Storage Cycle 2 Days in H_2O at 73 F 5 Days in Air, 100 F, 24% RH	
	Jeffersonville	Elgin	Jeffersonville	Elgin	Jeffersonville	Elgin
7	6380	5760	5800	5700	5920	5220
28	6320	7190	7280	7060	7890	7750
90	6040	8790	6950	8350	7870	8300
180	6270	9750	6630	8320	7770	9220
360	6810	10070	5840	8700	9360	9740

[a] 3- by 6-in. cylinders made with Elgin, Ill., gravel and rim-developing Jeffersonville limestone from Indiana (both 3/4-in. max. size); cement content 6.3 to 6.7 sk/cu yd; w/c ratio 4 1/2 gal/sk; slump 1 to 2 in.; cured 1 day in molds at 73 F, 100% RH, then to designated storage.

Test Results.—Test results are given in Table 8. Under all storage conditions the over-all strength and the rate of strength development in the Jeffersonville concretes were affected.

The specimens subjected to the wetting and drying cycle showed normal strength development for the first month, but failed to show any gain in strength between 28 days and 6 mo. Between 6 mo and 1 yr, the specimens began once more to gain in strength, becoming comparable to the Elgin concretes at 1 yr.

The specimens stored in cans over water at 100 F were more severely affected and did not gain significantly in strength between 7 days and 1 yr. The specimens stored in the moist room at 73 F were the most severely affected and showed a slow but steady decline in compressive strength from 28 days to 1 yr. At the end of the test period, the Jeffersonville concretes moist cured at 73 F had developed only two-thirds the strength of the comparable Elgin specimens. Testing will be continued to determine whether long-term strength loss occurs and if it is sufficient to affect the performance of field concrete.

DISCUSSION

Evaluation of Sampling and Testing Techniques

In any study of this type, one of the most difficult problems is that of obtaining representative samples. In this respect, the geologically oriented approach taken in this investigation proved valuable. By sampling a relatively small number of key sections, it was possible to determine the general character of the rocks in each of the formations exposed in the area. All of the stratigraphic horizons found to bear reactive rocks were identified in the initial sampling that encompassed only 22 sites. Supplementary sampling delineated the horizontal extent of the reactive beds and investigated possible lateral variations in rock characteristics.

The test program, involving the great number of samples necessary for adequate coverage of the thickness of rock involved, would not have been feasible without the special test methods which were developed. These simple tests, which require only a small amount of rock and permit the concurrent testing of large numbers of samples, proved to be ideally suited for a large-scale reconnaissance of this type. They do, however, necessitate certain precautions. Because the prism size is small in comparison to the body of rock itself, great care must be taken in sampling to insure that the samples are actually representative of the bed being tested. Although the same is true to some extent of concrete and mortar bar tests, it is possible in these cases to

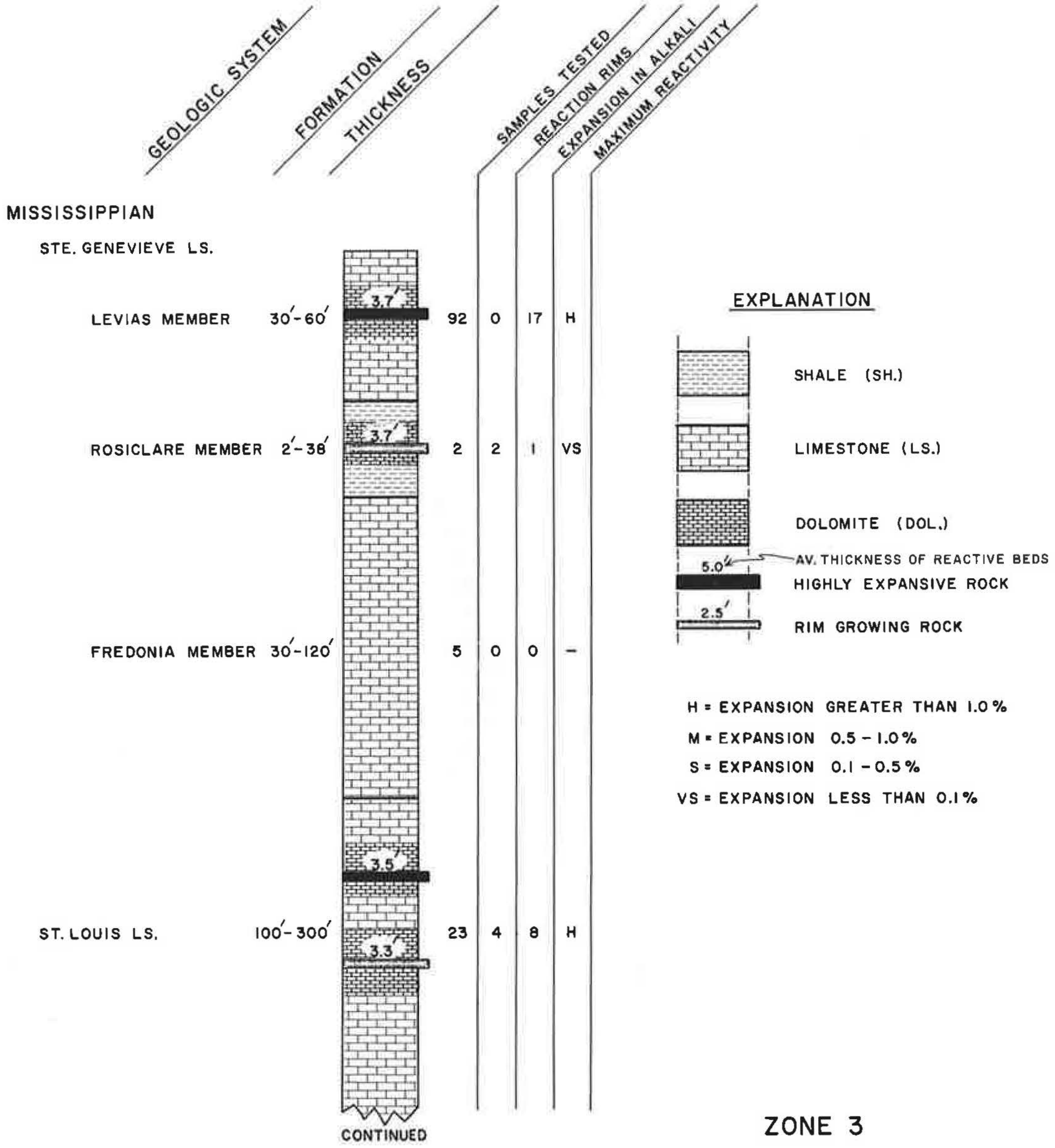


Figure 6. Columnar section showing distribution of reactive beds.

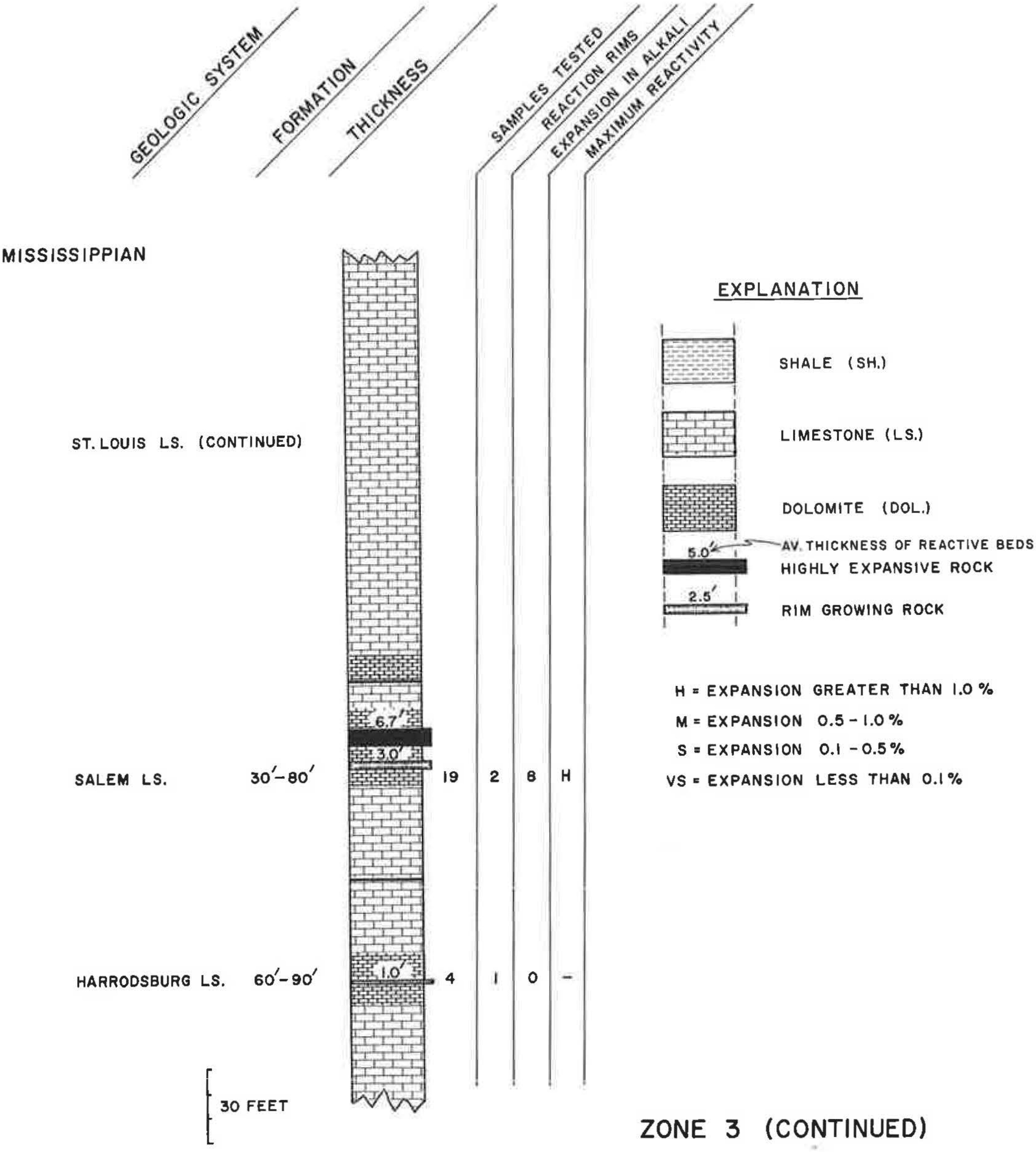


Figure 7. Columnar section showing distribution of reactive beds.

has been exposed to erosion for an extended period, there are many localities where bedrock is exposed or only thinly covered.

Wisconsin Till.—The Wisconsin till is the most recent and is a much thicker deposit than the Illinoian. The combined thickness of Wisconsin and earlier tills reaches as much as 550 feet. Exposures of bedrock are extremely rare in the portions of the state covered by the Wisconsin till.

The areas covered by the Illinoian and Wisconsin glaciers are shown on the geologic map (Fig. 1).

Distribution of Carbonate Rocks.—As is shown in the geologic cross-sections (Fig. 2), there are three major zones in the vertical sequence of rocks that outcrop in Indiana in which limestones and dolomites form the principal rock types. The production of carbonate aggregates is almost entirely confined to the rocks in these zones. Each of these zones contains one of the stratigraphic horizons cited by Patton (10) as holding rock which performed poorly in concrete. The approximate geographic areas in which rocks of each zone are quarried are shown in Figure 3.

Sample Collection

During the summer of 1959, 22 localities were sampled which included rocks from almost all of the strata exposed in each zone. Sampling was done on a bed-by-bed basis with additional samples taken from any bed which showed appreciable lateral variation within the limits of the outcrop. To avoid misinterpretation of this study as an evaluation of specific aggregate sources, sampling was largely confined to road-cuts, abandoned quarries, and natural exposures.

Although the initial sampling gave a good coverage of the vertical sequence of rocks, it was realized that a good deal of lateral variation probably existed in many of the formations sampled. Numerous additional exposures between the principal sections were therefore examined and sampled wherever significant variations in the nature of the rock were recognized. As a further check, the author obtained permission to study the fine collection of thin sections of carbonate rocks on file at the Industrial Minerals Section of the State Geological Survey in Bloomington. Because previous laboratory studies had shown that the reactive carbonate rocks all fell within a fairly narrow range of mineral compositions and textures, it was possible to differentiate quickly potentially reactive rocks from those which were obviously nonreactive. About 200 were selected as representative of the potentially reactive rocks in each formation, and the Geological Survey generously donated small samples of each for testing.

On the generalized columnar sections of the vertical sequences of rock exposed in each zone (Figs. 4-7) are shown the number of samples from each formation tested for chemical reactivity.

TESTING PROGRAM

Laboratory Tests for Reactivity

Inasmuch as the type of investigation envisioned called for the concurrent testing of a large number of samples, it was apparent that the testing of concrete specimens like those used by Swenson (1) and by Bisque and Lemish (2) in their early work would be cumbersome. Not only would there be an almost prohibitive number of specimens to be cast and stored but the large amounts of rock necessary would greatly complicate the sampling program. It was recognized that a need existed for the development of simple and rapid tests which could be carried out using relatively small quantities of rock. The results of these tests could later be confirmed by testing concretes made using representative reactive materials.

Test for Development of Reaction Rims.—The following test was designed to determine whether a rock would develop silicified rims in concrete:

Procedure.—Cubes ½ in. on a side were cut from each rock with a diamond saw. The cubes were then cast into 1- by 1- by 11¼-in. mortar bars made with graded Ottawa sand and a cement containing 0.06 percent Na_2O and 1.3 percent K_2O. Each bar con-

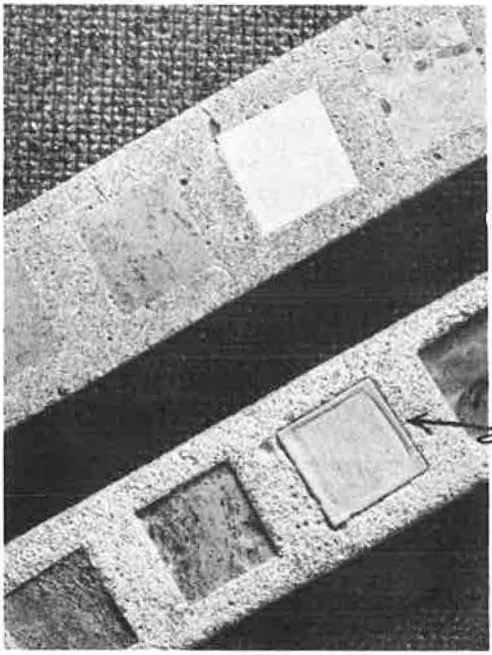


Figure 8. Rock cubes embedded in mortar bars. Development of reaction rims shown by acid etching of bars.

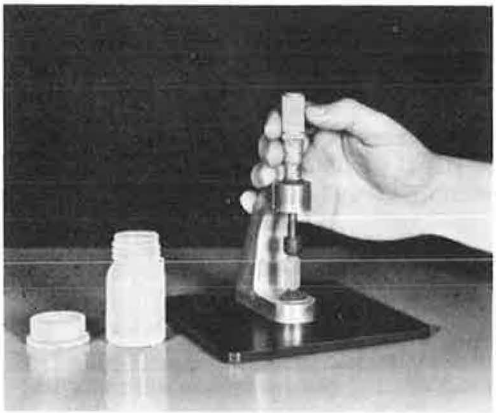


Figure 9. Simple test for measuring rock samples for expansion in alkali solution.

tained 12 aggregate cubes. The bars were stored over water in sealed containers at 100 F for 8 wk. They were then cut in half longitudinally with a diamond saw and one-half of the bar was etched with dilute HCl. The presence of reaction rims on the aggregate cubes was established by visual examination of the etched bars. Part of a typical test specimen is shown in Figure 8. In general, the rock is etched considerably below the level of the mortar. However, in the paste bordering reactive rock cubes there is a carbonated zone which etches to as great or greater depth as the interior of the rock. The rim itself is extremely resistant and remains at about its original level.

Test for Expansion.—Because the cause of distress in concrete containing these rocks had been found to be expansion of the coarse aggregate when exposed to cement alkalies, it was decided to test the aggregates themselves for expansion in alkaline solutions.

Procedure.—Small prisms were cut from each rock and exposed to a 1M NaOH solution. The presence and magnitude of expansion were determined by periodically measuring the prisms with a small comparator shown in Figure 9. This test was described in a previous publication (6).

Determinations were also made of the carbonate and clay mineralogy, insoluble residue content, and textural relationships for each rock in the test series as part of the research program on alkali-reactive carbonate rocks.

Test Results

Expansive Rocks.—Sixteen of the geologic formations exposed in Indiana were found to contain rock which expanded in 1 M NaOH solution. These formations and the ranges of expansions shown by the reactive samples tested are given in Table 1. Reactive rocks of this type were found throughout the vertical sequence of rocks and in each of the three zones of carbonate outcrop.

An appreciable number of the samples tested was found to be expansive in alkali. Table 1 shows that more than three-fourths of the reactive samples expanded less than 0.5 percent. The more highly reactive rocks were confined to limited portions of five formations: the Osgood, Salem, North Vernon, Ste. Genevieve, and St. Louis, the last being one of the three formations cited by Patton (10) as containing rocks with poor service records.

The expansive rocks were generally of poor physical quality, probably because of their high clay content. Figure 10 shows that greater than 80 percent of the rocks which expanded more than 0.5 percent contained more than 10 percent clay, and 7 of 17 contained more than 20 percent. Figure 10 also indicates that there is a minimum clay content necessary for reactivity (shown by the dashed line), and that this content increases as the carbonate fraction becomes more dolomitic. From a practical standpoint this is quite significant. Figure 11 shows that most of the expansive rocks in Indiana have high dolomite contents. Because these highly dolomitic reactive rocks were all found to have extremely high clay contents, there is a high probability that they would fail physical acceptance tests and be rejected as concrete aggregate.

Rim-Developing Rocks.—Nine formations contained rocks that developed reaction rims in concrete (Table 2). The pattern of distribution was much the same as that of the expansive rocks. It is interesting to note that each of the three formations listed by Patton was found to contain rim-developing rocks, with the St. Louis containing expansive rocks as well.

TABLE 1

FORMATIONS CONTAINING EXPANDING ROCKS

Formation	Expansion[a] (%)
Golconda	0.06
Kokomo	0.05 0.23 0.07 0.06 0.25 0.13
Laurel	0.11
Liston Creek	0.08 0.14
Louisville	0.05 0.13 0.27
Menard	0.25
Minshall	0.12
Mississinewa	0.14 0.22
Osgood	0.49 0.15 0.32 1.81 1.20 0.10 0.05
Providence	0.16
Rockford	0.09 0.06
Salem	0.05 0.24 1.46 0.07 0.24 0.03 0.04 0.06
Saluda	0.25
North Vernon (Beechwood member)	0.28
North Vernon (Silver Creek member)	2.00 0.56 0.20 0.45 0.74 4.88 0.18
North Vernon (Speed member)	0.05 4.05 2.22
Ste. Genevieve (Levias member)	0.17 0.13 0.11 3.06 0.07
Ste. Genevieve (Rosiclare member)	0.10
St. Louis	0.56 2.09 0.07 2.54 1.08 0.05 0.56 0.32

[a] In 1M NaOH solution during 30 weeks.

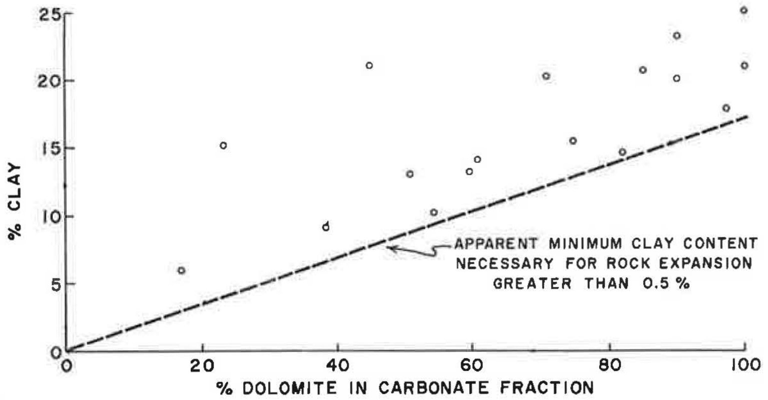


Figure 10. With increase in dolomite content, larger clay contents appear necessary for rock to show strongly expansive tendencies.

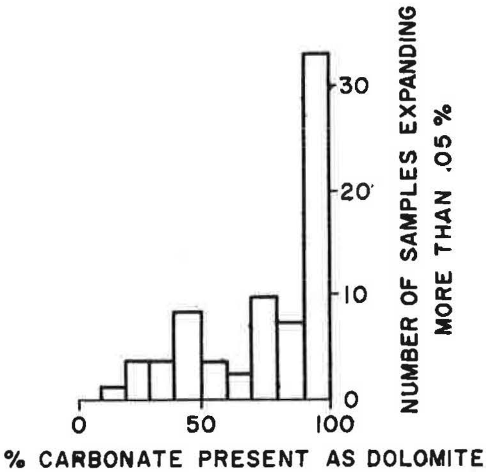


Figure 11. Most reactive rocks are highly dolomitic.

TABLE 2

FORMATIONS CONTAINING RIM-DEVELOPING ROCKS

Harrodsburg	Ste. Genevieve
Jeffersonville	(Rosiclare member)
Kenneth	Salem
Kokomo	St. Louis
Louisville	Whitewater

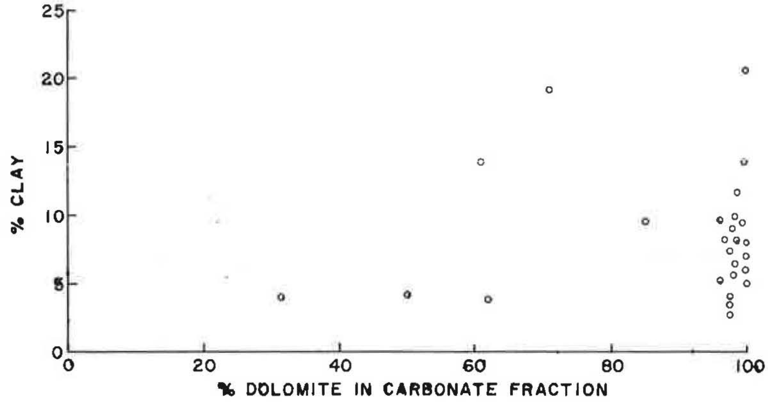


Figure 12. Rocks developing reaction rims tend to contain more dolomite and less clay than highly expansive rocks.

The rim-developing rocks were very similar to the expansive rocks in texture. The two types were often found interbedded and some expansive samples also developed weak reaction rims. The major difference between the two types of reactive rocks lies in their compositions. As is shown in Figure 12, the rim-developing rocks are generally highly dolomitic and contain appreciably less clay than expansive rocks of the same calcite-dolomite ratio. Almost all of the rim-developing rocks have clay contents that fall beneath the line in Figure 10 marking the minimum clay content necessary for expansion. The only rim-developing rocks that fall above this line also expanded and appear transitional between the two types. The rim-developing rocks as a class are physically superior to their expansive equivalents.

The test results for both the rim-developing and the expansive rocks are summarized on the columnar sections (Figs. 4-7).

INVESTIGATION OF STE. GENEVIEVE LIMESTONE

Of the five formations found to contain highly expansive rock, only one, the Ste. Genevieve limestone, is a significant source of concrete aggregate. Inasmuch as aggregate from this formation has an outstandingly good service record, the recognition of reactive beds in the Ste. Genevieve aroused considerable interest. Therefore, a detailed investigation of the rocks of this formation was conducted to determine whether the reactive material was potentially dangerous to the continued excellent service of this aggregate and to discover, if possible, the factors that had allowed the successful utilization of the reactive rock.

Field Studies

The Ste. Genevieve limestone is divided into three members: the Fredonia, the Rosiclare, and the Levias. As no reactive material had been found in the Fredonia member, and only one sample of quite low reactivity was found in the Rosiclare, this study was concentrated on the rocks of the Levias member.

In the summer of 1961, approximately 50 exposures of the Levias member were studied in the field. Twenty representative exposures were sampled on a bed-by-bed basis, yielding a total of 88 samples for laboratory study.

Laboratory Studies

Twenty-four of the samples, including rocks from 10 of the 20 sections sampled, contained dolomite. Tests for expansion in alkali showed 9 of the dolomitic samples to be reactive. These reactive rocks were found in 6 of the 20 exposures sampled. The gross mineral composition, thickness of the reactive beds, and expansions of the reactive samples are given in Table 3 and the areal distribution of the tested sections is shown in Figure 13.

Mode of Occurrence of Reactive Levias Rocks

Although the Levias shows rapid and extreme lateral variations, it is made up of a relatively small number of rock types. Relationships are confused, however, because in any given outcrop any of these rock types may be partially converted to dolomite and potentially reactive. The reactive rocks in the Levias, rather than occurring in a persistent bed or beds, are found in thin discontinuous deposits that cannot be traced laterally for any great distance and cannot be correlated between exposures.

Nature of Reactive Levias Rocks

The alkali-reactive rocks from the Levias are unusual because they contain much less clay than the reactive materials usually encountered. The rocks also differ from the other reactive Indiana carbonate rocks in that many are extremely compact and dense, probably as a consequence of the low clay content. Because the reactive Levias rocks are apparently physically sound, they probably would pass existing acceptance tests. The beds are thin and the reactive rocks are often interbedded with sound rock

TABLE 3

MINERALOGICAL COMPOSITION AND ALKALI REACTIVITY OF SPECIMENS FROM LEVIAS MEMBER OF STE. GENEVIEVE LIMESTONE

Sample	Thickness of Bed (ft)	Dolomite in Carbonate Fraction (%)	Insoluble Residue (%)	Expansion in 1 M NaOH (%)
61-2-2	6	23	4.5	0.10
61-2-4	12	17	4.7	0.04
61-2-6	4	51	14.1	0.36
61-6-2	3	58	6.5	0.25
61-9-3	7	78	6.3	0.05
61-10-2	1.5	34	6.2	0.11
61-14-1	3	36	4.6	0.09
61-16-6	2	39	8.7	0.09
61-16-7	4	10	8.7	0.05

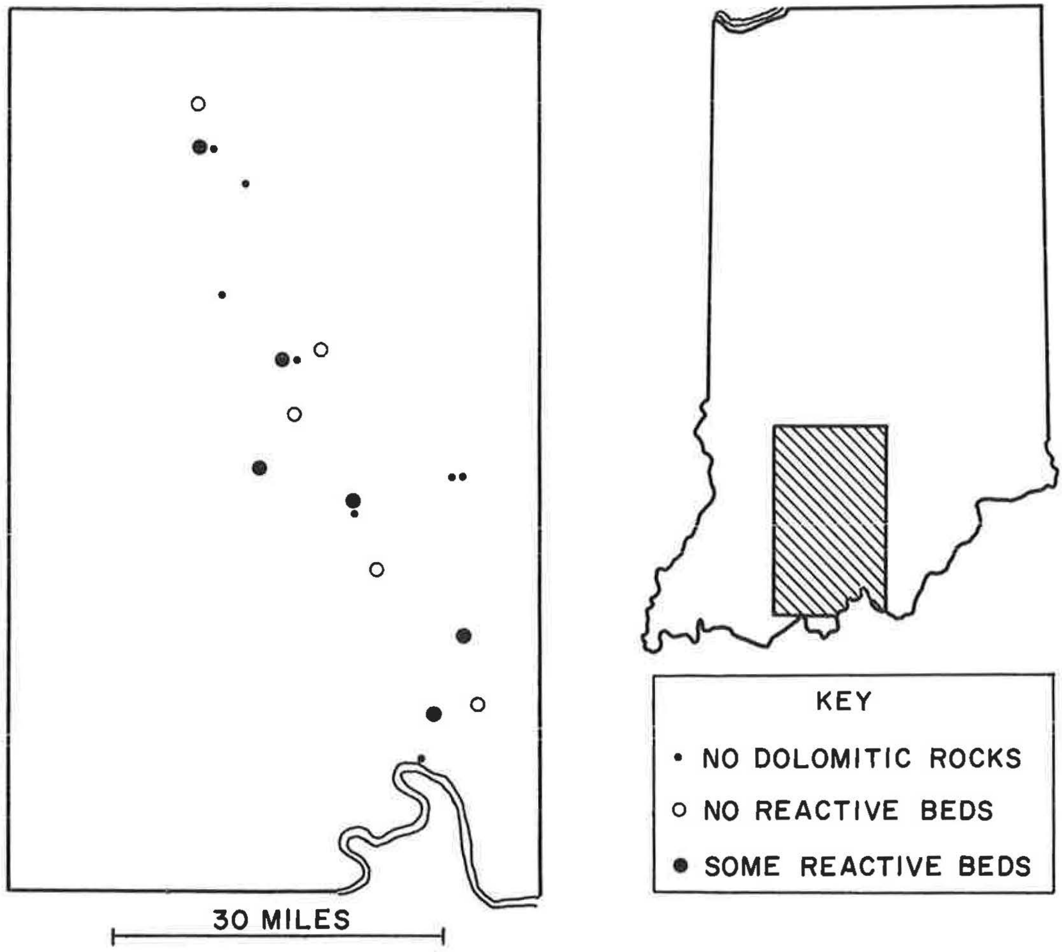


Figure 13. Thin reactive beds are randomly distributed throughout outcrop of Levias member of Ste. Genevieve limestone in Indiana.

material. It is likely, therefore, that the reactive material would pass undetected into concretes made with aggregate from quarries in the Levias.

Conclusions Regarding Investigation of Ste. Genevieve Limestone

Although one isolated sample of highly reactive rock was found in the initial sampling of the Levias, the general level of reactivity is relatively low. In addition, the reactive beds are thin and represent a very small proportion of the total Ste. Genevieve section. Probably this combination of generally low reactivity and dilution with sound rock permits the excellent performance of Ste. Genevieve aggregate in concrete. To check this hypothesis, three examples of expansive Levias rock were included in the aggregates used in the concrete tests described later. These tests indicated that even with a cement of high alkali content, the amount of dilution with sound aggregate that occurs in quarries now operating in the Ste. Genevieve is more than sufficient to reduce concrete expansion to an acceptable level. However, in some of the sections tested, a large proportion of the Levias rocks exposed were somewhat reactive. If a quarry opened in such a locality did not penetrate the nonexpansive rock of the underlying members to a sufficient depth to insure adequate dilution, some expansion might be produced if the material was used as concrete aggregate with a cement high in alkalies.

The excellent service record of the Ste. Genevieve reflects the fact that this potentially dangerous situation does not exist in any of the quarries now operating in the Ste. Genevieve.

CONCRETE AND MORTAR TESTS

Once the areal and stratigraphic distribution of the reactive rocks had been established, representative beds were selected for large-scale sampling. The rock was hand-quarried from the selected beds with every effort to secure rock like that initially sampled.

Tests of Expansion of Concretes Made with Expansive Rocks

Concrete tests were performed using six of the expansive rocks as coarse aggregate. The main purposes of these tests were: (a) to relate the expansion in alkali of the small rock prisms to that of laboratory concretes made with these rocks as coarse aggregate, and (b) to determine the degree of reactivity in the rock at which the laboratory concrete would be deleteriously affected.

The effects of variations in cement alkali content, air content, and of dilution with various proportions of essentially inert coarse aggregate were also investigated.

Description of Concrete Mixtures.—All mixtures were maintained at a nominal cement content of 6.0 sacks per cubic yard. The water content was adjusted to maintain a slump of 2 to 3 in. Sand constituted 38 percent of the absolute volume of aggregate and the maximum aggregate size was 1½ in.

Materials.—Three Type I cements purchased in the Chicago area were used. The chemical analyses, specific gravity, and fineness of these cements are listed in Table 4.

The fine aggregate was a natural sand from Elgin, Illinois, and the coarse aggregates were selected reactive crushed stone from Indiana and an inert gravel from Elgin, Illinois. Grading, specific gravity, and absorption of these aggregates are given in Table 5.

Specimen Preparation.—Four 3- by 3- by 11¼-in. prisms were cast from each batch. Each reactive aggregate was tested at 0, 25, 50, and 75 percent dilution with inert Elgin gravel aggregate, and each of the dilutions was tested with each of the three cements.

Curing.—Immediately after casting, the specimens were stored under wet burlap covered with a polyethylene sheet. After 20-24 hr the prisms were removed from the molds, their lengths were measured, and two specimens from each batch were placed in sealed containers over water at 100 F. The remaining two specimens from each batch were stored at 73 F and 100 percent RH.

Testing.—Prisms were measured for length immediately after removal from the molds, weekly for a month, bi-weekly for two additional months, and monthly thereafter.

TABLE 4

CHEMICAL ANALYSES, SPECIFIC GRAVITY AND FINENESS OF CEMENTS USED IN LABORATORY CONCRETE TESTS OF EXPANSIVE COARSE AGGREGATES

Lot No.	Analytical Result (%)												Sp. Gr.	Fineness		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Tot. Alk., as Na_2O	Loss on Ign.	Insol. Resi-due	Mn_2O_3		Blaine	Wagner	-325 (%)
20070	22.10	4.36	2.86	62.75	3.10	2.36	0.14	1.14	0.89	0.93	0.03	0.10	3.18	3240	1800	92.0
20071	21.02	5.60	2.97	64.04	2.68	2.34	0.32	0.43	0.60	0.50	0.04	0.30	3.19	3140	1760	90.6
20072	20.54	5.59	2.28	63.50	3.23	2.48	0.13	0.16	0.24	1.43	0.20	0.74	3.18	3680	1850	91.6

TABLE 5

CHARACTERISTICS OF AGGREGATES USED IN LABORATORY CONCRETES

Aggregate	Grading (% retained)									Bulk Sp. Gr., S.S.D.	Absorp.[a] (% by wt.)
	1½ In.	¾ In.	⅜ In.	No. 4	No. 8	No. 16	No. 30	No. 50	No. 100		
Elgin, Ill., sand[b]	—	—	—	0	18	33	57	87	95	2.645	2.25
Elgin, Ill., gravel	0	50	75	100	—	—	—	—	—	2.651	2.00
Expansive coarse aggregates	0	50	75	100	—	—	—	—	—	—	—
Ste. Genevieve, 19999	—	—	—	—	—	—	—	—	—	2.655	1.95
Osgood, 20000	—	—	—	—	—	—	—	—	—	2.550	6.00
Ste. Genevieve, 20001	—	—	—	—	—	—	—	—	—	2.485	5.20
Ste. Genevieve, 20002	—	—	—	—	—	—	—	—	—	2.570	2.06
St. Louis, 20007	—	—	—	—	—	—	—	—	—	2.680	1.55
North Vernon, 20024	—	—	—	—	—	—	—	—	—	2.660	1.50

[a] 24 hr. [b] Fineness modulus 2.90.

Test Results.—Test results are summarized below and representative data are shown graphically in Figures 14-20. Complete test data are given in the Appendix.

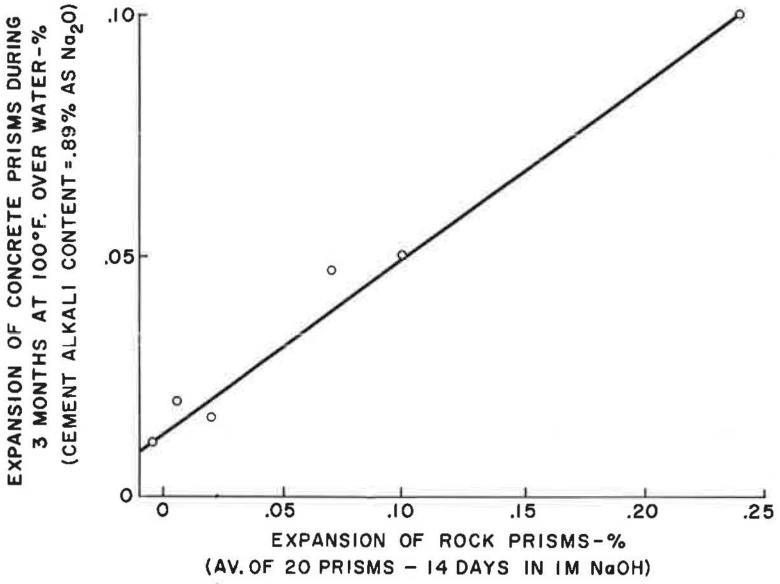


Figure 14. Correlation between expansion of rock prisms and concretes made with these rocks as aggregate.

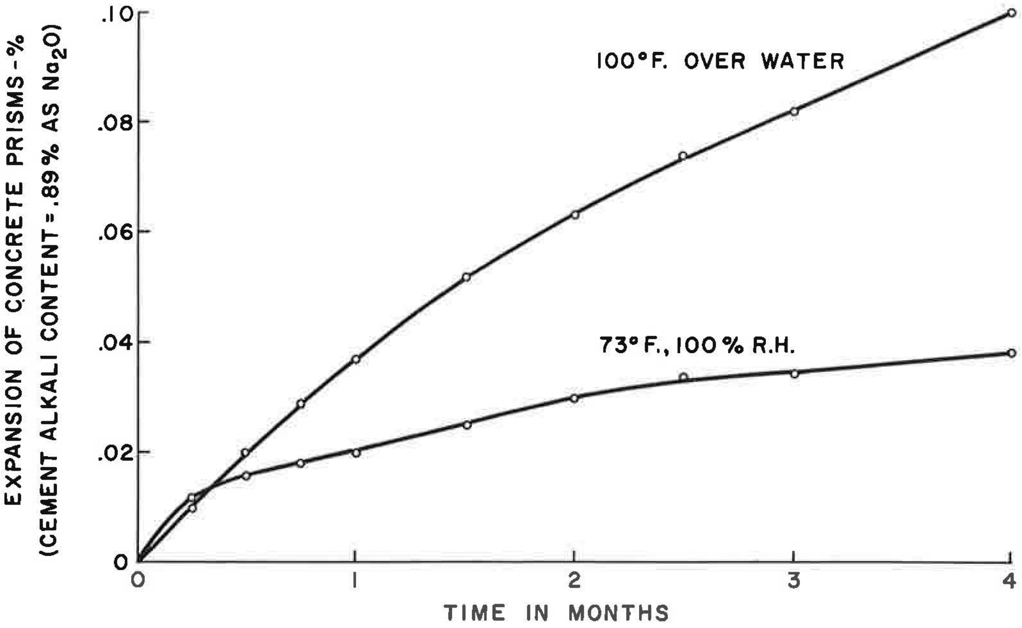


Figure 15. Rate of expansion of concrete was greatly accelerated by storage at higher temperature.

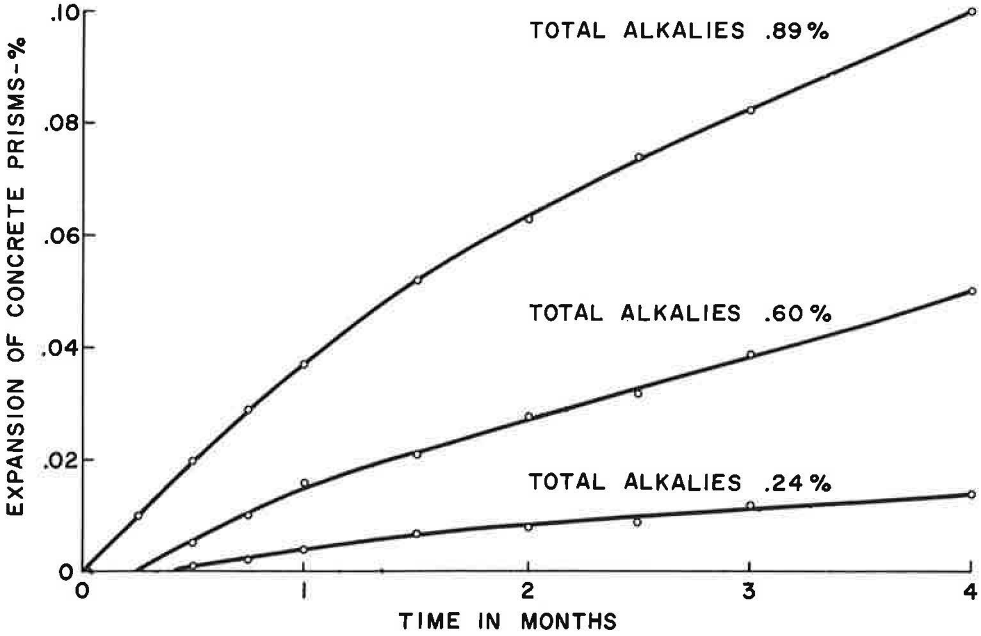


Figure 16. Rate of expansion of concrete is greatly influenced by alkali content of cement.

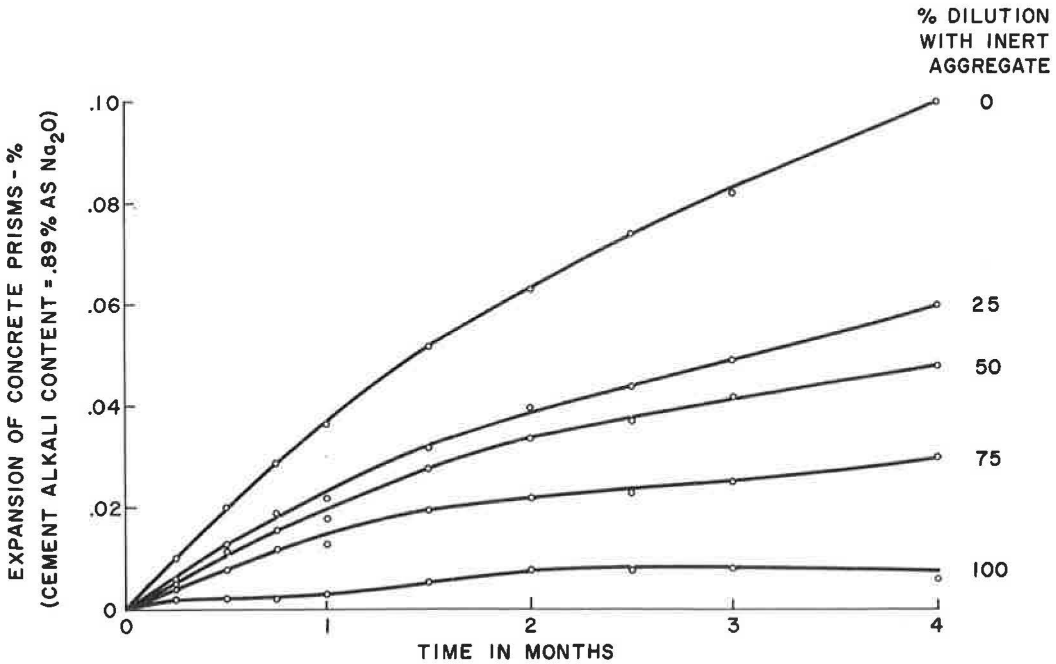


Figure 17. Dilution reduces concrete expansion by amount roughly proportional to amount of inert aggregate used.

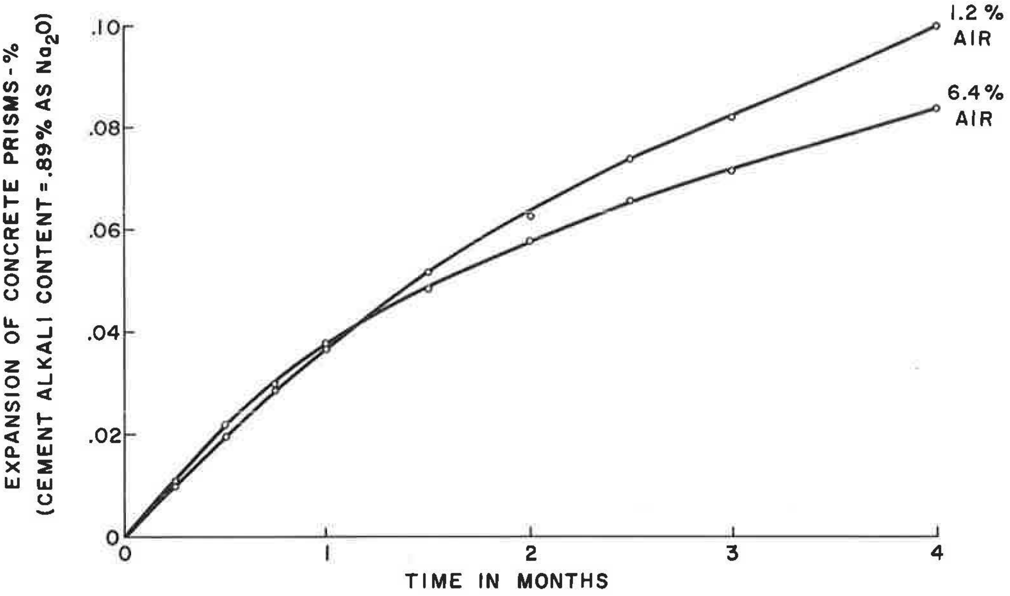


Figure 18. Air entrainment has no appreciable effect on expansion of concrete prisms.

1. Relation Between Expansion of Rock Prisms and Concretes Made Using These Rocks as Coarse Aggregate—The data from these tests indicate good correlation between the average expansion of a large number of rock prisms and expansions of concretes containing the rocks as aggregate. Figure 14 shows the 14-day average expansion of the rock prisms plotted against the expansion of the corresponding concretes after 3-mo storage.
2. Effect of Storage Conditions—Storage in cans over water at 100 F produced a more rapid expansion than storage in a moist room at 73 F and 100 percent RH, and the correlation between rock and concrete expansions was slightly better for specimens stored in cans (Fig. 15).
3. Effect of Cement Alkali Content—As Swenson and Gillott (5) found, the rate of expansion seems to be a direct function of cement alkali content (Fig. 16).
4. Effect of Dilution with Inert Coarse Aggregate—Dilution reduced expansion by an amount roughly proportional to the amount of inert aggregate used (Fig. 17).
5. Effect of Air Entrainment—The effect of air entrainment was studied in only one case. The air-entrained samples expanded at a slightly less rapid rate than their non-air-entrained counterparts (Fig. 18).

Mortar Bar Tests with Expansive Aggregates

Each of the six expansive aggregates was also tested by the Mortar Bar Expansion Test (ASTM C 227-61T) for potential alkali reactivity with the three cements used in the concrete tests.

Test Results.—Under a criterion that expansion greater than 0.05 percent at 3 mo indicates deleterious chemical reaction (ASTM C 33), the three most expansive aggregates failed the mortar bar test with the cement of 0.89 percent alkali content. On this basis the most highly reactive of the aggregates also caused deleterious expansion with the cement containing 0.60 percent total alkalies (Table 6).

Discussion.—These data differ from the findings of Swenson (1), who observed that although concrete prisms made with reactive Kingston, Ontario, aggregate expanded rapidly, mortar bars made with the same cement and aggregate showed only moderate expansions. Figure 19 shows that all mortar bars made with the reactive Indiana materials expanded more than the equivalent concrete prisms. The reason for this difference is not known and additional research is being conducted to study this question.

As is shown in Figure 20, the correlation between mortar bar expansion and the expansion of the rock prisms is good. This correlation indicates that the mortar bar test, ASTM

TABLE 6

EXPANSIVE ROCKS ALSO FOUND REACTIVE IN MORTAR BAR TESTS

Formation	Lot No.	Expansion, 3 Months (%)		
		Cement 20070[a]	Cement 20071[b]	Cement 20072[c]
Ste. Genevieve	19999	0.054	0.025	0.019
Osgood	20000	0.025	0.014	0.016
Ste. Genevieve	20001	0.035	0.019	0.018
Ste. Genevieve	20002	0.024	0.012	0.012
St. Louis	20007	0.101	0.053	0.026
North Vernon	20024	0.053	0.027	0.019
Elgin, Ill.	—	0.027	0.013	0.015

[a] Total alkali 0.89%.
[b] Total alkali 0.60%.
[c] Total alkali 0.24%.

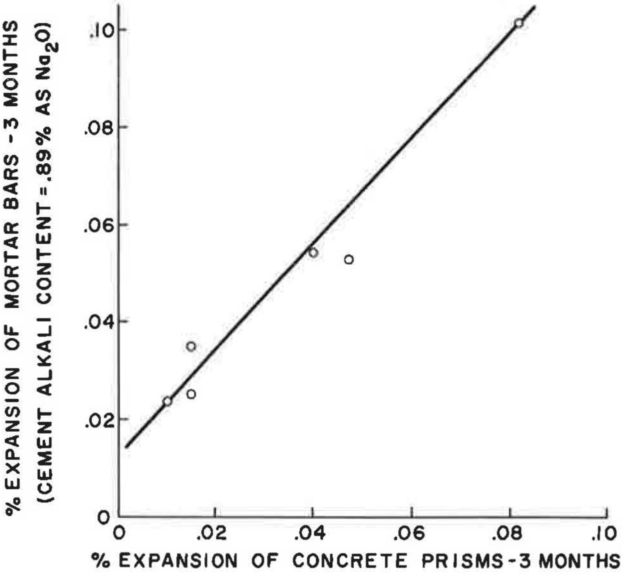


Figure 19. Expansive rocks produced slightly greater expansion in mortar bars than in corresponding concrete prisms.

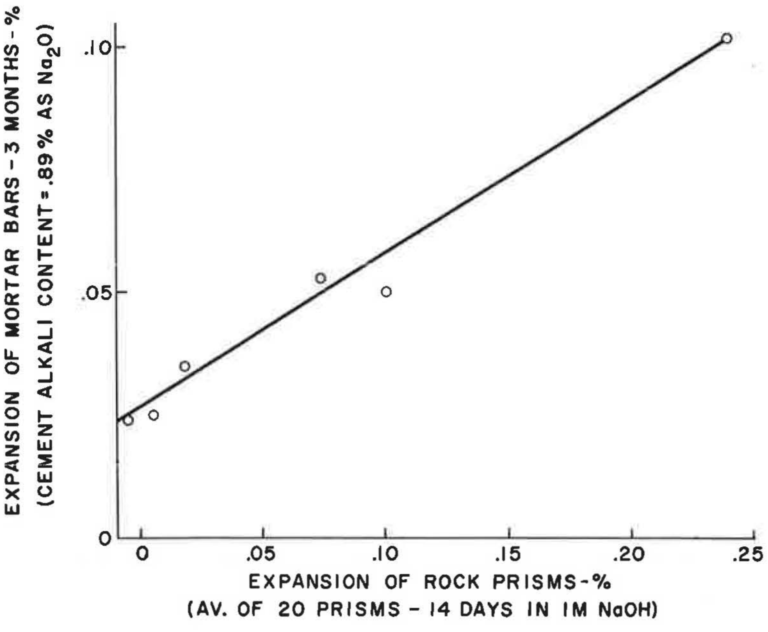


Figure 20. Expansion of rock prisms correlates well with that of corresponding mortar bars.

take much larger samples, and by using sample splitting techniques, achieve a more representative sampling.

If the necessity for careful sampling is recognized, however, these small-scale tests can be very useful tools. The correlation with concrete and mortar bar tests is quite good and a test for reactivity can be made in a fraction of the time that these tests would require.

Possible Utilization of Marginally Reactive Aggregate

The reactive rocks identified in Indiana showed expansions ranging from practically nothing to almost 5.0 percent. Although it is beyond the scope of this paper to attempt to define the lower limit of expansion that would produce deleterious results in field concrete, it appears obvious that many of the Indiana rocks are only marginally reactive. It seems prudent to investigate methods by which these marginal materials might safely be used in concrete.

The work of Swenson (1) showed that additions of pozzolanic materials or lithium salts, both somewhat effective in controlling the alkali-siliceous aggregate reaction, have no appreciable effect on the alkali-carbonate rock reaction. Similarly, although the expansion of affected concrete is dependent on the alkali content of the cement, measurable expansion might take place even with cements of low alkali content.

The remedial measure that seems to hold the most promise is that of dilution with inert aggregate materials. Unlike the alkali-siliceous aggregate reaction, in which there is a "pessimum" amount of reactive material, the expansion is decreased in the alkali-carbonate rock reaction by an amount roughly proportional to the percentage of dilution with inert material.

In most known occurrences, the reactive beds constitute only a small percentage of the rocks exposed, and the level of reactivity is for the most part low. In these cases, control would simply be a matter of making sure that adequate dilution and mixing took place in quarrying and crushing. In those rare instances where the percentage of reactive materials is high, the reactive rocks might still be safely utilized if dilution were coupled with the use of low alkali cement.

Correlation of Test Results with Field Service Records

The Expansive Rocks.—Although the reactive rocks are numerous in Indiana, there are few known cases of concrete damage in that area resulting from the expansion of alkali-reactive carbonate rocks. Due to their poor physical quality, most of the reactive materials in Indiana would probably never be used as concrete aggregate because aggregates of better physical quality are available. In those instances where the reactive rocks are physically sound, the level of reactivity is normally low, the reactive beds are thin, and the degree of dilution with inert aggregate occurring in the quarrying operation apparently is usually sufficient to reduce concrete expansions to within tolerable limits.

The Rim-Developing Rocks.—Attempts to correlate the test data on the rim-developing rocks with the available service records are complicated by several factors. The rim-developing rocks are often interbedded with closely related expansive rocks. In addition, many of these rocks were among those found by Sweet (9) to be highly susceptible to frost damage. However, because several of the rim-developing rocks do have extremely poor service records in concrete, future research plans call for intensified field and laboratory study of these rocks to determine whether their poor performance can be related to the processes that bring about the development of reaction rims.

SUMMARY

This study indicated that standard geologic field methods are well suited to large-scale surveys of the type described. The small-scale laboratory tests developed for this investigation provided a rapid indication of reactivity, and the results of these tests correlated well with those of conventional concrete and mortar bar tests.

Laboratory concrete studies, as well as field experience with the Ste. Genevieve limestone, indicate that many of the marginally reactive materials could be safely utilized as concrete aggregates through such measures as dilution with inert aggregate and the use of low alkali cement.

Although the reactive rocks were abundant in Indiana and have caused some damage to field concrete, such factors as exclusion of the reactive materials from concrete due to poor physical characteristics, generally thin deposits, and low over-all reactivity have combined to prevent the reactive rocks from becoming a major problem.

ACKNOWLEDGMENTS

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Appendix

EXPANSION OF LABORATORY CONCRETES[a]

Concrete Characteristics						Expansion (%)											
						100 F Over Water						73 F, 100% RH					
Coarse Agg.	Dilution (%)	W/C (gal/sk)	Cement Factor (sk/cu yd)	Net Air (%)	Slump (in.)	7 Days	28 Days	3 Mo	6 Mo	12 Mo	18 Mo	7 Days	28 Days	3 Mo	6 Mo	12 Mo	18 Mo
(a) Cement 20070 (Total Alkalies, as Na_2O, 0.89%)																	
Elgin	0	4.7	5.9	1.2	1.7	0.002	0.003	0.008	0.008	0.009	0.010	0.008	0.007	0.011	0.008	0.009	0.008
19999	0	5.0	5.9	1.2	1.6	0.007	0.022	0.044	0.058	0.074	0.080	0.010	0.017	0.027	0.031	0.042	0.046
20000	0	5.4	5.9	1.2	2.2	0.000	0.004	0.015	0.022	0.028	0.033	0.012	0.013	0.019	0.022	0.025	0.028
20001	0	4.7	5.9	1.2	2.5	0.008	0.010	0.015	0.016	0.019	0.020	0.013	0.015	0.021	0.020	0.022	0.023
20002	0	5.1	6.1	1.2	2.4	0.004	0.006	0.010	0.011	0.012	0.012	0.006	0.008	0.012	0.012	0.010	0.012
20007	0	5.0	5.9	1.2	1.3	0.010	0.037	0.082	0.118	0.146	0.160	0.012	0.020	0.034	0.041	0.052	0.057
20024	0	5.2	5.9	1.2	1.3	0.010	0.024	0.042	0.051	0.056	0.060	0.011	0.016	0.026	0.032	0.038	0.041
19999	25	5.0	5.9	1.2	1.9	0.008	0.022	0.040	0.054	0.066	0.072	0.011	0.014	0.023	0.026	0.030	0.034
19999	50	5.0	5.9	1.2	2.1	0.008	0.018	0.029	0.038	0.041	0.046	0.010	0.014	0.022	0.024	0.027	0.031
19999	75	5.0	6.0	1.2	2.8	0.006	0.010	0.018	0.022	0.026	0.028	0.009	0.012	0.018	0.018	0.020	0.023
20000	25	5.4	5.8	1.2	2.7	0.001	0.004	0.012	0.016	0.020	0.024	0.008	0.008	0.014	0.014	0.017	0.020
20000	50	5.7	5.7	1.2	1.8	0.004	0.006	0.014	0.018	0.022	0.023	0.010	0.010	0.016	0.015	0.018	0.020
20000	75	5.1	5.9	1.2	2.5	0.002	0.005	0.010	0.010	0.012	0.014	0.008	0.008	0.014	0.014	0.015	0.016
20001	25	4.8	5.5	1.2	1.6	0.010	0.013	0.018	0.016	0.020	0.023	0.014	0.015	0.020	0.016	0.018	0.018
20001	50	5.1	5.9	1.2	2.8	0.008	0.010	0.015	0.016	0.019	0.020	0.012	0.010	0.016	0.015	0.015	0.016
20001	75	5.1	5.9	1.2	2.0	0.006	0.007	0.012	0.012	0.014	0.016	0.010	0.008	0.014	0.011	0.012	0.012
20002	25	5.0	6.1	1.2	1.8	0.006	0.006	0.011	0.010	0.010	0.011	0.005	0.004	0.010	0.006	0.007	0.008
20002	50	4.9	6.0	1.2	2.2	0.003	0.004	0.010	0.011	0.012	0.014	0.008	0.006	0.012	0.008	0.008	0.008
20002	75	4.8	6.0	1.2	2.1	0.005	0.007	0.012	0.013	0.014	0.015	0.008	0.006	0.012	0.008	0.010	0.009
20007	25	5.0	5.8	1.2	1.8	0.006	0.022	0.049	0.068	0.073	0.079	0.011	0.016	0.030	0.035	0.048	0.052
20007	50	5.0	5.9	1.2	2.3	0.006	0.018	0.042	0.055	0.064	0.070	0.012	0.014	0.026	0.026	0.032	0.033
20007	75	4.9	5.9	1.2	2.1	0.005	0.013	0.025	0.032	0.040	0.042	0.008	0.008	0.018	0.019	0.024	0.026
20024	25	5.1	5.9	1.2	1.7	0.006	0.016	0.030	0.035	0.040	0.041	0.010	0.012	0.022	0.026	0.032	0.035
20024	50	5.1	5.8	1.2	1.7	0.005	0.012	0.024	0.030	0.034	0.036	0.010	0.012	0.022	0.024	0.028	0.030
20024	75	4.9	5.9	1.2	1.7	0.004	0.014	0.019	0.020	0.022	0.024	0.010	0.013	0.020	0.018	0.020	0.022
20007	0	4.4	5.9	6.4	1.7	0.011	0.038	0.072	0.102	0.122	0.132	0.012	0.024	0.042	0.053	0.068	0.074
20007	25	4.3	5.9	6.0	1.2	0.008	0.023	0.044	0.063	0.073	0.080	0.010	0.018	0.031	0.040	0.052	0.056
20007	50	4.3	5.9	6.3	1.5	0.010	0.024	0.044	0.054	0.063	0.067	0.006	0.016	0.027	0.030	0.038	0.044
20007	75	4.3	5.9	5.9	1.2	0.009	0.015	0.026	0.033	0.038	0.040	0.010	0.014	0.022	0.022	0.026	0.028
(b) Cement 20071 (Total Alkalies, as Na_2O, 0.60%)																	
Elgin	0	4.6	6.0	1.2	1.8	-0.002	0.004	0.004	0.006	0.006	0.007	0.006	0.006	0.008	0.006	0.005	0.006
19999	0	5.1	6.0	1.2	1.7	-0.002	0.012	0.026	0.038	0.051	0.058	0.008	0.012	0.017	0.017	0.022	0.024
20000	0	5.2	5.9	1.2	1.1	-0.010	0.004	0.004	0.010	0.016	0.020	0.010	0.010	0.014	0.014	0.017	0.020
20001	0	4.6	6.0	1.2	1.6	0.000	0.007	0.009	0.010	0.012	0.012	0.008	0.010	0.012	0.012	0.012	0.012
20002	0	5.0	6.2	1.2	1.6	-0.002	0.001	0.003	-0.001	0.002	0.002	0.004	0.005	0.006	0.004	0.004	0.004
20007	0	4.8	6.0	1.2	1.1	0.000	0.016	0.039	0.063	0.082	0.090	0.008	0.010	0.018	0.020	0.028	0.032
20024	0	5.2	6.0	1.2	0.9	-0.002	0.010	0.024	0.033	0.041	0.048	0.005	0.008	0.014	0.018	0.022	0.024
19999	25	5.0	5.9	1.2	1.7	0.002	0.008	0.018	0.030	0.040	0.046	0.010	0.013	0.020	0.022	0.026	0.027
19999	50	5.0	5.9	1.2	2.3	-0.002	0.002	0.009	0.016	0.024	0.027	0.010	0.014	0.017	0.016	0.020	0.020
19999	75	4.9	6.0	1.2	2.3	-0.002	0.002	0.008	0.013	0.018	0.022	0.006	0.008	0.010	0.008	0.010	0.010
20000	25	5.2	6.0	1.2	1.0	-0.009	-0.006	0.001	0.005	0.012	0.017	0.018	0.016	0.021	0.019	0.022	0.024
20000	50	4.9	5.9	1.2	1.6	-0.003	0.001	0.005	0.008	0.014	0.015	0.008	0.006	0.010	0.009	0.012	0.013
20000	75	5.0	6.0	1.2	2.3	-0.004	-0.002	0.001	0.001	0.006	0.006	0.008	0.007	0.010	0.008	0.011	0.011
20001	25	4.7	5.6	1.2	1.0	0.001	0.004	0.006	0.005	0.008	0.009	0.008	0.009	0.013	0.012	0.014	0.014
20001	50	4.6	6.1	1.2	1.2	-0.002	-0.002	0.004	0.004	0.006	0.007	0.009	0.008	0.011	0.008	0.009	0.009
20001	75	4.6	6.0	1.2	2.2	-0.001	0.002	0.004	0.004	0.007	0.007	0.008	0.006	0.010	0.010	0.012	0.010
20002	25	5.1	6.1	1.2	2.5	-0.004	-0.004	0.002	0.003	0.004	0.004	0.010	0.008	0.012	0.007	0.008	0.008
20002	50	5.0	6.0	1.2	2.9	-0.004	-0.004	0.000	0.000	0.002	0.000	0.008	0.006	0.010	0.009	0.008	0.008
20002	75	4.9	6.0	1.2	2.2	-0.003	-0.002	0.002	0.001	0.003	0.004	0.006	0.006	0.008	0.006	0.006	0.007
20007	25	4.9	5.8	1.2	1.5	-0.002	0.004	0.002	0.040	0.052	0.060	0.008	0.010	0.018	0.016	0.021	0.022
20007	50	4.9	5.9	1.2	1.6	-0.002	0.004	0.014	0.022	0.031	0.034	0.006	0.006	0.013	0.014	0.018	0.014
20007	75	4.9	6.0	1.2	2.8	-0.001	0.002	0.008	0.011	0.018	0.019	0.006	0.004	0.010	0.004	0.008	0.008
20024	25	5.0	6.0	1.2	1.9	-0.002	0.006	0.016	0.020	0.028	0.032	0.010	0.010	0.018	0.015	0.017	0.020
20024	50	5.1	6.0	1.2	2.0	0.000	0.004	0.014	0.015	0.022	0.024	0.006	0.008	0.014	0.012	0.015	0.015
20024	75	5.0	5.9	1.2	1.8	-0.001	0.002	0.008	0.010	0.013	0.013	0.007	0.006	0.012	0.012	0.014	0.014
(c) Cement 20072 (Total Alkalies, as Na_2O, 0.24%)																	
Elgin	0	5.0	5.9	1.2	2.1	0.002	0.000	0.002	0.004	0.006	0.006	0.008	0.006	0.007	0.004	0.006	0.007
19999	0	5.2	5.9	1.2	1.6	0.000	0.003	0.008	0.009	0.016	0.022	0.006	0.006	0.010	0.008	0.010	0.012
20000	0	5.5	5.9	1.2	1.0	-0.005	-0.003	0.002	0.012	0.020	0.024	0.018	0.017	0.020	0.017	0.022	0.026
20001	0	4.7	5.9	1.2	2.3	0.004	0.006	0.010	0.012	0.014	0.016	0.007	0.007	0.008	0.006	0.006	0.008
20002	0	5.0	6.2	1.2	1.7	-0.002	0.002	0.005	0.005	0.005	0.005	0.004	0.006	0.006	0.002	0.004	0.004
20007	0	5.1	5.9	1.2	1.6	-0.002	0.004	0.012	0.020	0.025	0.030	0.009	0.010	0.014	0.017	0.022	0.026
20024	0	5.2	5.9	1.2	1.0	0.000	0.004	0.008	0.013	0.019	0.023	0.008	0.011	0.014	0.012	0.016	0.018
19999	25	5.1	5.9	1.2	2.8	0.000	0.004	0.011	0.013	0.019	0.024	0.004	0.006	0.007	0.006	0.008	0.010
19999	50	5.1	5.9	1.2	2.4	-0.001	0.000	0.005	0.008	0.015	0.018	0.009	0.011	0.013	0.010	0.014	0.015
19999	75	5.1	5.9	1.2	2.5	0.003	0.004	0.008	0.008	0.012	0.015	0.012	0.012	0.012	0.008	0.010	0.012
20000	25	5.4	5.9	1.2	2.2	-0.007	-0.006	0.000	0.007	0.014	0.020	0.014	0.018	0.020	0.020	0.024	0.026
20000	50	5.4	5.9	1.2	2.3	-0.002	-0.001	0.006	0.011	0.016	0.020	0.016	0.016	0.018	0.018	0.022	0.024
20000	75	5.4	5.9	1.2	2.4	0.000	0.000	0.004	0.006	0.010	0.012	0.010	0.012	0.014	0.013	0.016	0.017
20001	25	5.2	5.8	1.2	1.5	0.002	0.003	0.006	0.004	0.006	0.008	0.010	0.010	0.011	0.008	0.010	0.010
20001	50	5.0	5.9	1.2	2.2	0.003	0.004	0.006	0.006	0.010	0.012	0.006	0.008	0.009	0.006	0.008	0.008
20001	75	5.0	5.9	1.2	2.5	0.002	0.002	0.006	0.006	0.009	0.012	0.008	0.008	0.010	0.008	0.011	0.011
20002	25	5.3	6.0	1.2	1.9	-0.002	0.000	0.003	0.008	0.006	0.006	0.005	0.006	0.010	0.010	0.010	0.010
20002	50	5.1	6.0	1.2	1.9	-0.001	0.003	0.006	0.006	0.004	0.004	0.006	0.007	0.009	0.006	0.006	0.006
20002	75	5.0	5.9	1.2	2.7	-0.002	0.002	0.006	0.007	0.005	0.007	0.006	0.007	0.009	0.008	0.009	0.009
20007	25	5.0	5.9	1.2	2.3	-0.002	0.003	0.010	0.016	0.021	0.024	0.005	0.008	0.012	0.014	0.018	0.020
20007	50	5.0	5.9	1.2	1.6	-0.002	0.002	0.004	0.004	0.004	0.006	0.004	0.004	0.006	0.004	0.004	0.004
20007	75	5.0	5.9	1.2	2.0	-0.002	0.000	0.002	0.005	0.003	0.004	0.010	0.008	0.011	0.006	0.008	0.008
20024	25	5.1	5.8	1.2	1.0	-0.003	0.004	0.009	0.014	0.018	0.020	0.004	0.006	0.009	0.010	0.012	0.014
20024	50	5.1	5.8	1.2	2.0	-0.003	0.002	0.008	0.009	0.012	0.016	0.006	0.006	0.010	0.010	0.011	0.013
20024	75	5.0	5.9	1.2	2.9	-0.004	0.002	0.006	0.008	0.008	0.010	0.004	0.008	0.009	0.010	0.010	0.012

[a] Each value is average of two 3 × 3 × 11¼-in. concrete prisms.

A Survey for Reactive Carbonate Aggregates in Virginia

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Respectively, Geologist and Highway Research Engineer, Virginia Council of Highway Investigation and Research

•THE DISCOVERY of alkali-reactive carbonate rocks in a Virginia quarry producing aggregates otherwise acceptable under Virginia Department of Highways Specifications (8) immediately suggested the necessity of determining the occurrence of these materials in other producing quarries. In addition to the need to know the location of reactive aggregates, the possibility of correlating the expansive behavior of such rocks with stratigraphy or mineralogy was also of considerable interest.

This paper presents data obtained from tests on rock samples taken in a survey of active quarries furnishing carbonate aggregates for concrete used by the Virginia Department of Highways. The shaded portion of the map in Figure 1 delineates those areas of Virginia underlain by carbonate rocks. Quarries which produce stone used in the Virginia highway system and which were sampled for this study are marked by the solid dots. The areas underlain by limestone and dolomite and the quarries producing carbonate aggregates are concentrated in the Valley and Ridge Physiographic Province. Only two quarries producing carbonate material for concrete are outside this area; they are located in the Arch or Everona marble in the Piedmont portion of the state.

The primary objectives of the survey were to determine: (a) the frequency of occur-

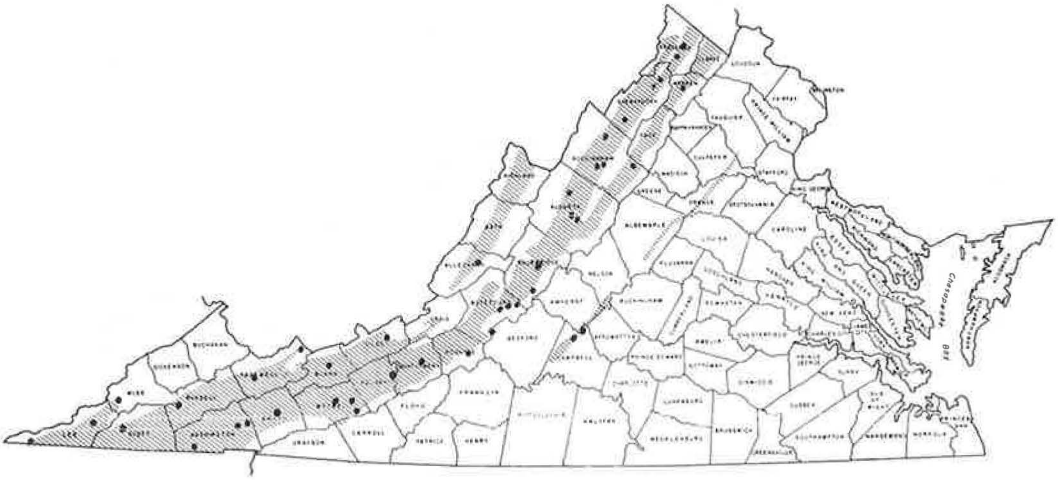

Figure 1. Location of quarries sampled. Shaded areas represent extent of carbonate rocks exposed in Virginia; solid dots show individual quarry locations.

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rence and volume of reactive carbonate aggregates being produced in Virginia, (b) the geographic and stratigraphic distribution of this material, (c) the lithologic characteristics of the expansive rocks, and (d) any correlations which might exist between mineralogic composition and expansive or other reactive behavior.

Investigations of the samples included measurement of susceptibility to alkali reaction by the prism test (5), formation of rims in mortars as discussed by Bisque and Lemish (1, 2, 3), determination of carbonate mineralogy and insoluble residue, and studies of thin sections.

The approach adopted in the survey was to gather limited samples from a large number of quarries. These preliminary samples would serve to satisfy the aforementioned objectives as well as to indicate the need for more extensive and detailed sampling of quarries containing reactive beds.

METHOD OF SAMPLING

Prior to sampling, a rapid survey of each of the quarries shown in Figure 1 was made to determine the different lithologies exposed in the workings. Oriented samples were collected from each lithologic type where quarry walls were accessible; where they were inaccessible, samples were taken from blast material. A total of 224 samples were collected from 42 quarries. The number of samples taken from any particular quarry varied from 2 to 15, depending on the size of the quarry and the degree of variation between the beds exposed.

Table 1 gives the geologic formations exposed in the quarries, together with the total number of samples taken from each formation and the number of quarries involved. This listing indicates that more of the carbonate aggregates used in the state are quarried from the Beekmantown than from any other formation, with the Elbrook, Shady (Tomstown) and Conococheague formations being nearly equal and next in importance as sources of supply.

TABLE 1

STRATIGRAPHIC DISTRIBUTION OF SAMPLES[1] TAKEN IN STATEWIDE SURVEY

Period	Formation or Member	No. of Samples	Quarries Involved
Mississippian	Newman Seam	7	1
Devonian	Licking Creek	5	1
Ordovician	Lowville (Moccasin)	10	2
	Ward Cove-Whitten (undifferentiated)	16	2
	Edinburg (Athens)	13	5
	Effna (Holston)	2	1
	Lincolnshire (Lenoir)	3	1
	Whistle Creek	1	1
	New Market-Five Oaks (Mosheim)	10	6
	Beekmantown (Upper Black Beds)	13	3
	Beekmantown (other)	55	13
Cambrian	Conococheague	23	3
	Elbrook (plus Honaker)	29	4
	Rome (Waynesboro)	6	1
	Shady (Tomstown)	25	6
Pre-Cambrian (?)	Arch or Everona	6	2

[1] Contains only those formations sampled and is not meant to be a complete geologic column.

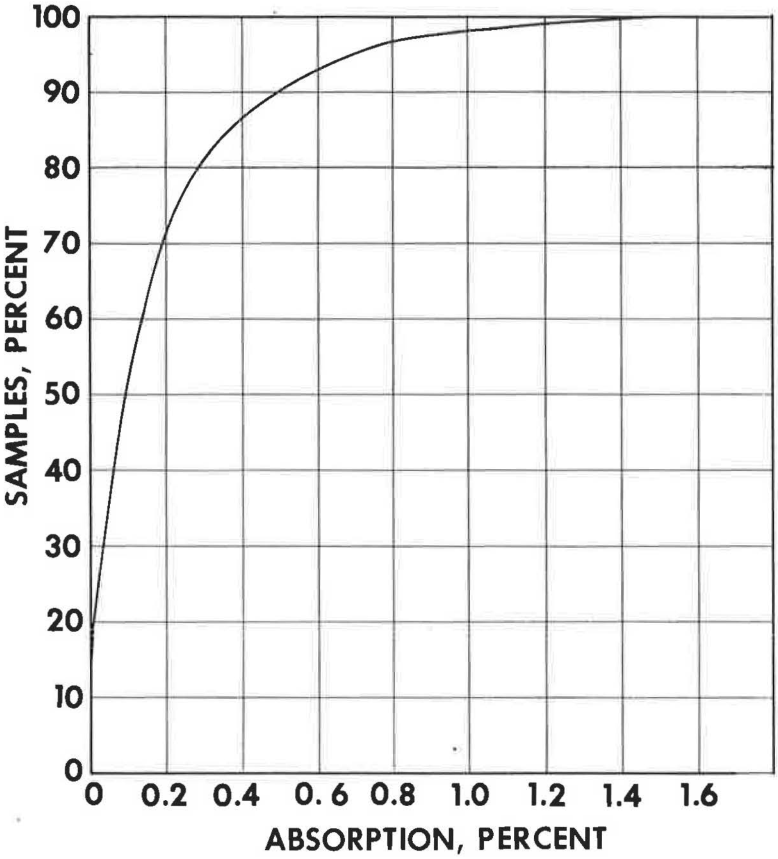

Figure 2. Cumulative curve showing percent of samples vs percent absorption.

ANALYSES OF SAMPLES

Physical Characteristics

Because of the large number of quarries involved and the preliminary nature of the survey, only small hand specimens weighing approximately 1,000 gm were collected. Thus, conventional measures of physical soundness could not be obtained. The vast majority of the rock samples, both expansive and nonexpansive, would, however, be considered physically acceptable. An appreciation of the general quality of the materials may be gained from the fact that each quarry produces concrete aggregate which, at the time of sampling, was required to meet the limits in Table 2.

The specific gravity and absorption after 24 hr of soaking were determined for each sample. The bulk specific gravities fell within the range 2.65 to 2.85. Approximately 98 percent of the samples had absorptions less than 1 percent (Fig. 2).

TABLE 2

SPECIFICATION REQUIREMENTS FOR GRADE A CONCRETE AGGREGATES USED IN VIRGINIA

Test	Max. Loss	
	Condition	(%)
Abrasion Resistance (AASHO T 62)	500 rev.	35
$MgSO_4$ Soundness (AASHO T 104)	5 cycles	8

Mineralogy of Samples

Carbonate Mineralogy. --The percentage of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) present in the carbonate fraction of each sample was determined by X-ray diffraction, following the method of Tennant and Berger (11). Samples of

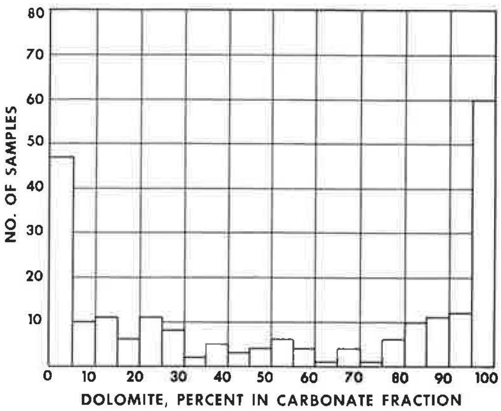

Figure 3. Distribution of carbonate compositions of test samples.

the ledge rock were prepared for X-ray analysis by hand grinding approximately 5 gm of sample to pass a No. 200 sieve. The powder was then transferred to a steel ball mill and tumbled for 17 hr. Most of the resulting powder passed a No. 325 sieve. This powder was packed into a standard well-type holder and the surface was made smooth with a glass plate. Nickel-filtered copper radiation with a 1° divergence slit and 0.003-in. receiving slit was used for the analyses. Scanning was done at a rate of 2° of 2 θ per min for the 10° interval between 25° and 35° where the major peaks for calcite and dolomite appear. Areas under the peaks were measured with a planimeter and the ratios for the dolomite/calcite peaks were compared to a standard curve constructed previously to determine the percentages of each mineral in the carbonate fraction. This procedure, if properly and carefully performed, has been shown by Diebold, Lemish and Hiltrop (4) to be accurate to within 1 mole percent.

The distribution of carbonate compositions (Fig. 3) indicates that relatively pure limestones and dolomites are more prevalent in this group of samples than are mixtures of the two in nearly equal proportions. This carbonate distribution is similar to that noted previously in the literature for a suite of carbonate rocks of similar age in Illinois (6). The apparent scarcity of the intermediate compositions is not well understood at the present time.

Insoluble Residues.—The noncarbonate portion of the Virginia limestones and dolomites is generally composed of acid-insoluble silicates, such as quartz and clays. The

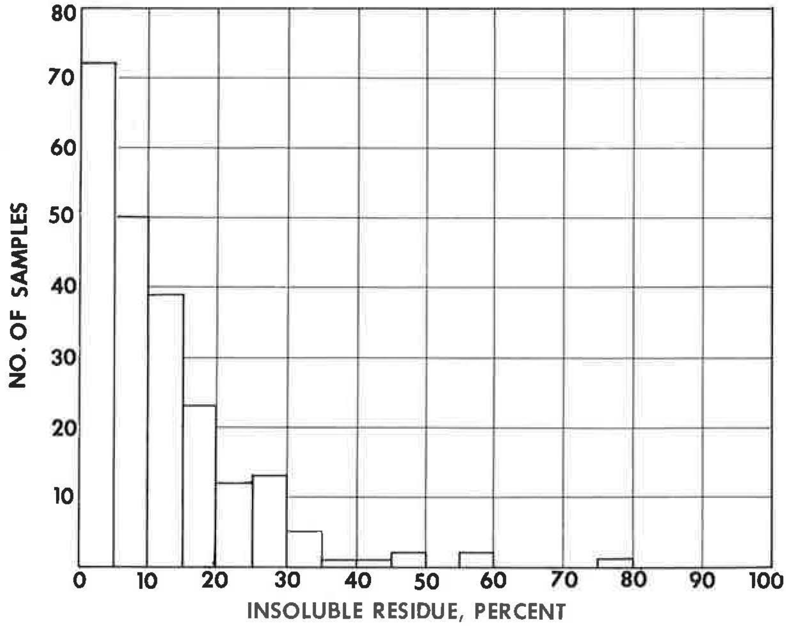

Figure 4. Distribution of insoluble residues determined for test samples.

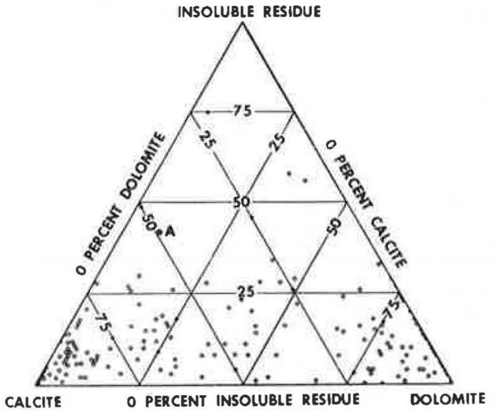

Figure 5. Ternary plot of composition of test samples.

percentages of insoluble residue were obtained by weighing a pulverized sample of the rock and treating it with an excess of concentrated HCl. When reaction was complete the residue was washed, dried, and weighed. Figure 4 shows the distribution of determined insoluble residues by percent intervals. More than 50 percent of the samples fell in the intervals between 0 and 10 percent.

The ternary plot in Figure 5 shows the percentages of insoluble residue, calcite and dolomite of a sample by a single point. The amount of each constituent in a sample is proportional to the perpendicular distance from the point to the side of the triangle opposite the constituent. For example, point A in Figure 5 represents a sample containing 42 percent insoluble residue, 49 percent calcite, and 9 percent dolomite.

Thin-Section Descriptions. --Thin sections were made from 79 of the samples including both expanding and nonexpanding rocks. Study with the petrographic microscope indicates that, based on mineralogy and texture, four major types or end members can be distinguished. These are listed in the following together with a discussion of the predominant characteristics observed in each group. Photomicrographs of each type are shown in Figure 6.

1. Well-crystallized dolomite. These rocks consist principally of interlocked dolomite grains with distinct grain boundaries and little calcite or insoluble material between dolomite crystals. In the whole group the dolomite crystal size ranges from about 10 to 60 μ, but in any one example the grain size is nearly constant. Primary sedimentary features are generally not visible and the insoluble residue content of these rocks is low.

2. Micrograined calcite. Individual calcite grains in these sections, aside from recrystallized veins or patches, are predominantly very fine grained, ranging from nearly submicroscopic to about 5 μ. Variations within this dense fabric are due to variations in the aggregations of these grains. Fossils, oolites, pellets, and transported fragments are the most common of these aggregations. When distinct aggregations are not evident, the extremely fine-grained calcite produces a very dense fabric almost devoid of primary sedimentary features. Insoluble content ranges from less than 1 to 50 percent.

3. Calcite and dolomite in discrete zones. Thin sections of banded or laminated rock types may show the boundaries that separate layers dominantly dolomite from those dominantly calcite. These boundaries may be gradational or abrupt in character. Many of the abrupt or sharp boundaries are marked by the presence of stylolites. Within the layers the character of the material closely resembles that described in 1 and 2 .

4. Interspersed calcite and dolomite. Discrete, well-crystallized dolomite rhombs, surrounded by finer-grained calcite, are characteristic. The dolomite grains appear clear or zoned with inclusions in thin section. The calcite, because of its finer grain size and because the insoluble materials are concentrated in this fraction, is usually cloudy or dark in color. These rocks are characteristically high in insoluble residue.

RESULTS OF TESTS FOR REACTIVITY

Expansion

From each of the samples collected one prism was made and tested by the method developed by Hadley (5) for measuring the alkali-induced expansion of carbonate rocks.

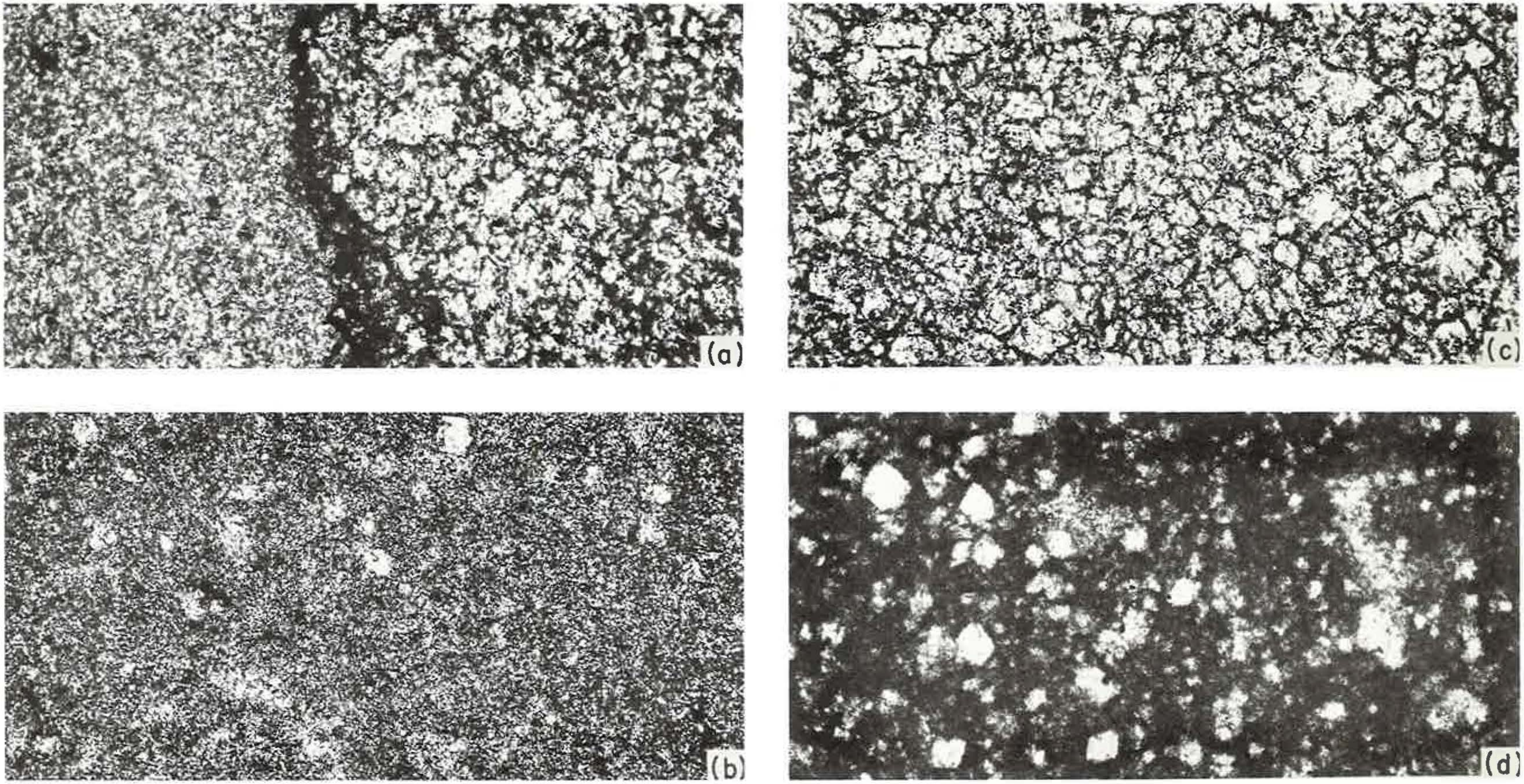

Figure 6. Photomicrographs (50X) of typical Virginia carbonate rocks: (a) medium-grained, well-crystallized dolomite with no primary sedimentary features evident; (b) fine-grained calcite with sizeable amounts of clay and clay-size quartz intermixed and a few recrystallized patches evident; (c) laminated rock with alternating zones of fine calcite and coarse dolomite and sharp boundary more prevalent than gradational types; and (d) discrete dolomite rhombs surrounded by matrix of fine-grained calcite and clay.

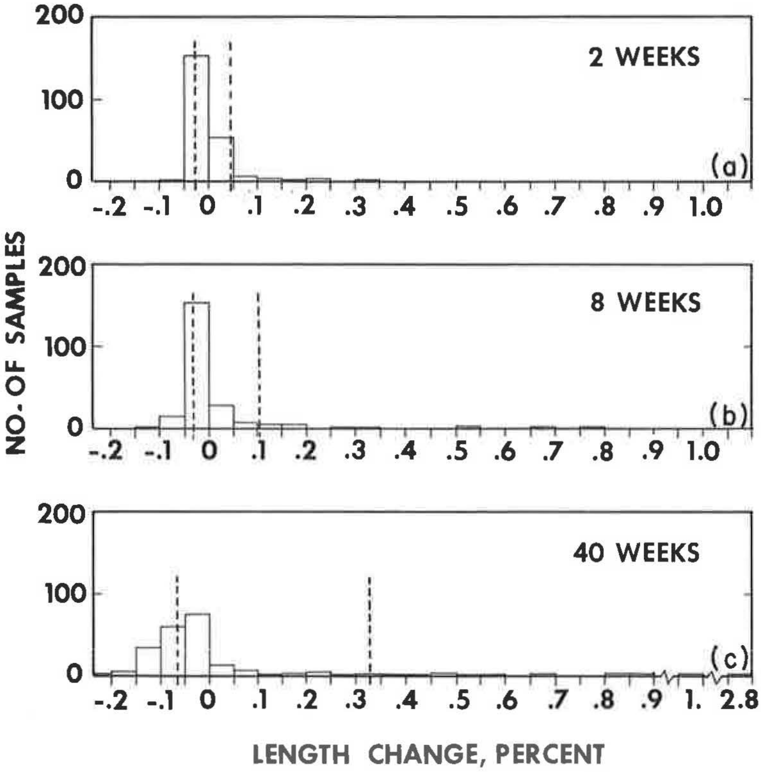

Figure 7. Number of samples vs length change at 2, 8, and 40 wk for 224 test samples. Vertical dashed lines represent average expansion and contraction.

The procedure involved cutting 1¼- by ¼- by ¼-in. prisms normal to the bedding from the rock samples and grinding conical apices on each end. The prisms were measured in a length comparator, soaked in distilled water until they reached equilibrium length and transferred to a polyethylene bottle containing 30 ml of 1.0 N NaOH solution. The prisms were removed and measured at 1-wk intervals up to 8 wk, and at 4-wk intervals thereafter.

Results of the prism measurements are shown graphically in Figure 7a, b and c for ages of 2, 8, and 40 wk, respectively. Several important aspects of length change are brought to light in these graphs; (a) the length changes, whether expansion or contraction, are progressive with time; (b) average expansion is nearly an order of magnitude greater than average contraction at ages of 8 wk or greater; and (c) the total number of rocks that contract in the NaOH solution is much greater than the number that expand.

Figure 8 shows the expansion curves of two typical samples each from those rocks showing very high, high, and moderate expansions. The general shape of the individual curves seems to indicate that expansion in most cases can be detected at soaking times of 2 to 4 wk. Expansion measurements taken to an age of 12 mo yielded only a few prisms in which expansion began after 4 wk in NaOH.

As length change data accumulated, it became evident that more intensive testing of certain quarries was needed. This work is now in progress. Detailed sampling of all beds for prism tests and hand picking and crushing of selected beds for fabrication of concrete test samples have been accomplished for several quarries. Results of this work to date have substantiated the results of the original survey. Prism expansions of up to 6.5 percent with no visible cracks at 30 wk and concrete expansions in excess of 0.1 percent at 1 yr have been obtained for this material.

The status of the prism test (5) should be emphasized at this point. At present, it is not an accepted test by any standardizing agency but is one of several currently

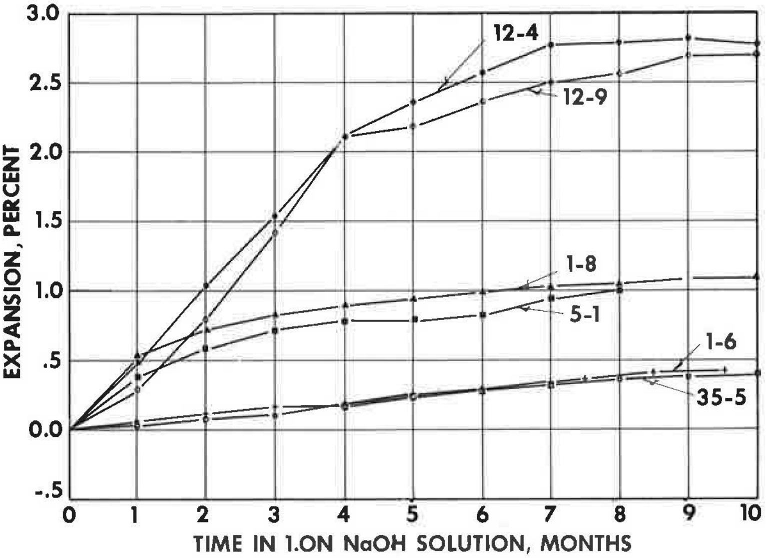

Figure 8. Representative expansion curves.

under investigation. Investigations, directed toward correlating the prism test with concrete behavior and especially toward determining a threshold point for deleterious reaction, are under way. Consequently, prism test results should be viewed at this time in a relative rather than an absolute sense.

Rim Formation

In addition to the expansive alkali-induced reaction, rim growth in concrete aggregates is of current interest. Bisque and Lemish (1, 2, 3) first noted rims or silica-rich zones in the aggregate particles near the aggregate—cement paste interface of some Iowa concretes. These rims appeared in positive relief when the concrete was sawed and etched in hydrochloric acid. Subsequently Mather et al. (7) described rims in concrete aggregates which are frequently discolored and which are preferentially etched in acid and appear in negative relief.

To investigate the tendency of Virginia aggregates to form rims, ½-in. cubes were cut from all of the 224 samples under study. These were embedded in mortar bars, conforming to the requirements of ASTM C 227, with cement having an alkali content of 0.95 calculated as equivalent Na_2O. The bars were stored in closed containers over water at a temperature of 37.8 ± 1.7 C. After 8 wk, each mortar bar was sawed parallel to its length so that each half contained one-half of each of the embedded cubes. One of the sawed surfaces was etched in 3N HCl. Rims were found in 25 of the 224 cubes. All but two of these were negative rims. The composition of the rim-forming rocks and the type of rims formed can be seen in Figure 9. Figure 10 shows a negative and a positive rim from this group.

The distribution of the rim-growing samples in the composition plot in Figure 9 shows that: (a) the negative rims are virtually limited to high calcite rocks, (b) the insoluble residue contents are generally low, and (c) the limited evidence in the case of positive rims points to compositions high in dolomite. A check for rim vs expansion showed that six of the 25 rimmed rocks also expanded, and that two of these reached expansions in excess of 0.1 percent after 6 mo. Because the percentage of the rim-growing rocks that expanded is about the same as the percentage of all the samples that expanded, no relationship between rim growth and expansion appears to exist. It should be noted also that no effects, either deleterious or beneficial, have been proven attributable to rim growth at this time.

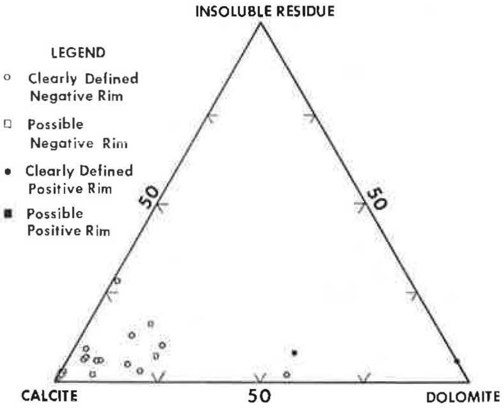

Figure 9. Composition of rim-forming rocks.

RELATIONSHIPS OF REACTIVITY TO COMPOSITION AND STRATIGRAPHY

An understanding of the relationships between expansive alkali reactivity and other intrinsic properties of carbonate rocks is essential to an understanding of the fundamental cause of the observed deleterious reaction. Figures 11 and 12 were plotted to determine whether any relationship exists between expansive reactivity and either carbonate mineralogy or insoluble residue content. The number of samples of a given composition is plotted as in Figures 3 and 4 along with a superimposed dashed line showing the number of samples of that composition which expanded in the prism test.

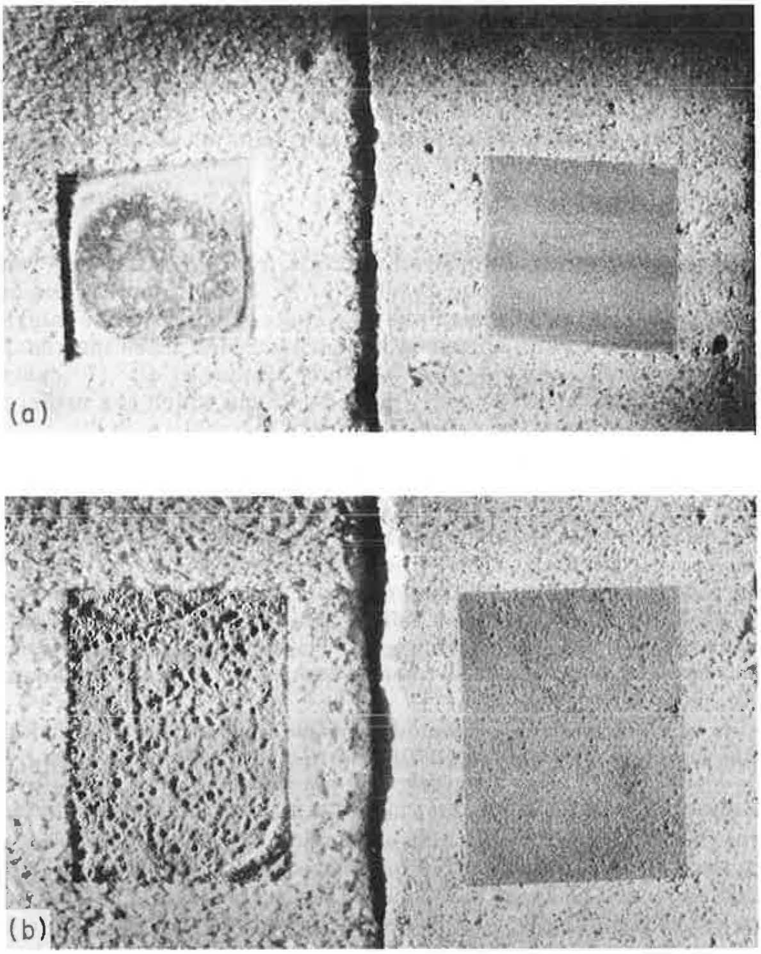

Figure 10. Close-ups of sawed cubes in mortar bars comparing acid-etched and non-etched halves: (a) negative rim, and (b) positive rim.

The correlation of expansion with certain intermediate mixtures of calcite and dolomite appears fairly good in Figure 11. A puzzling aspect of the distribution of expanding samples in Figure 11 is the lack of such samples in the rocks composed of 70 to 90 percent dolomite in the carbonate fraction. Of those rocks in the 10 to 70 percent dolomite range, 42.7 percent expanded, compared to only 6.7 percent in the 0 to 10 and 70 to 100 percent dolomite ranges. The correlation between expansive rock and insoluble residue percent shown in Figure 12 may be even more significant. Those rocks containing 15 to 35 percent insoluble residue have a much higher percentage of expanding prisms than do those outside of these limits.

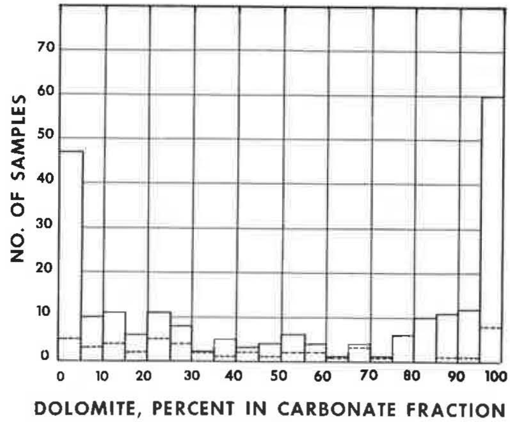

Figure 11. Distribtuion of calcite and dolomite contents of all samples. Number of rocks within each interval which expanded in the prism test is indicated by dashed line.

From the standpoint of total composition, a more comprehensive view of the relationship of expanding samples to all the samples tested is evident in the ternary diagrams in Figures 13, 14 and 15. Figure 13, like Figure 5, shows the ternary composition of each of the 224 test samples. In addition to the compositions, the diagram indicates the samples that expanded in the prism test in contrast to those that either contracted or remained constant. Figure 14 shows the compositions of those samples which expanded more than 0.2 percent at 6 mo. This 0.2 percent figure was arbitrarily adopted as a value large enough to cause

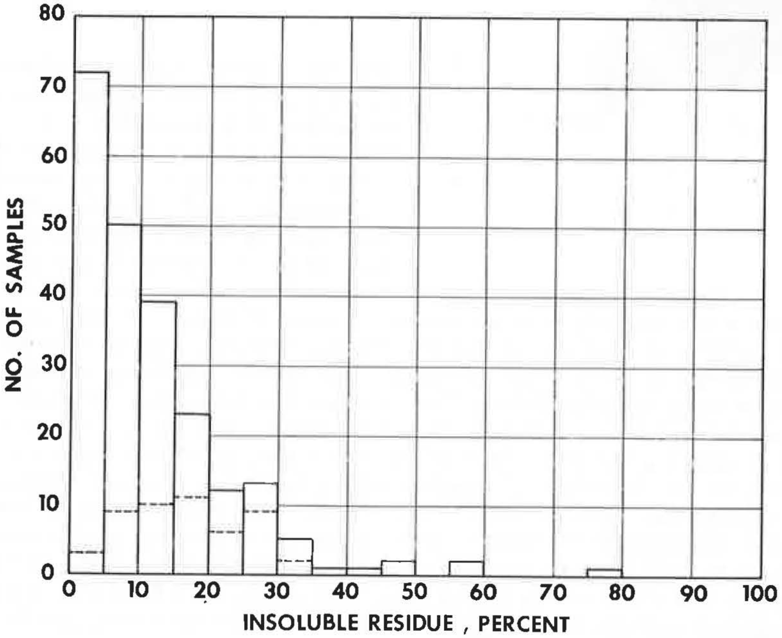

Figure 12. Insoluble residue contents of all samples. Number of samples within each interval which expanded in prism test is indicated by dashed line.

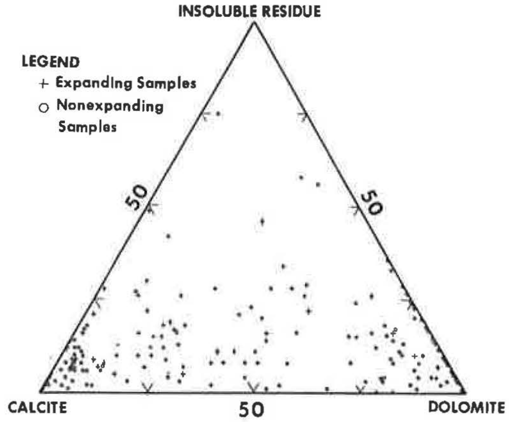

Figure 13. Three-component diagram of 224 test samples, showing which samples expand in the prism test at 6 mo and which did not.

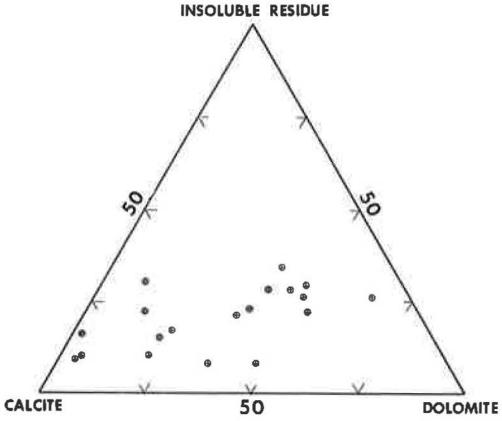

Figure 14. Composition of all samples under test which expanded 0.2 percent or more at 6 mo.

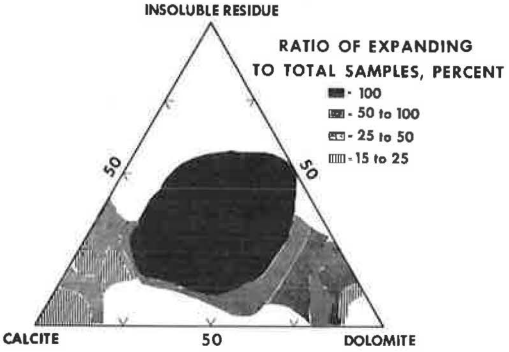

Figure 15. Contoured diagram of distribution of ratios of expanding samples to total samples, determined for 400 equal area increments of ternary plot.

TABLE 3

DISTRIBUTION BY FORMATION OF ROCK SAMPLES EXPANDING MORE THAN 0.2 PERCENT AT 6 MONTHS

Period	Formation or Member	No. of Samples	Quarries Involved
Mississippian	Newman Seam	1	1
Ordovician	Lowville (Moccasin)	4	2
	Edinburg (Athens)	3	2
	Beekmantown (Upper Black Beds)	11	3
Cambrian	Shady (Tomstown)	1	1

concern. Table 3 gives the distribution by formation of the samples that expanded more than 0.2 percent at 6 mo. From this tabulation it is evident that the most reactive material is concentrated in three stratigraphic units, the Lowville, Edinburg and Upper Beekmantown all of Ordovician age. It is interesting to note that most of the reactive rocks reported to date from other areas have been from Ordovician strata. Figure 15 is a contoured plot showing the composition field for various percentage values of reactive samples in the total samples falling in that portion of the diagram. The ternary field was divided into 400 equal increments using standard triangular coordinate graph paper. Counts were made in the 400 small triangles formed by the 5 percent lines. Points on a line were counted in both triangles sharing that line. The percentage of samples showing expansion was plotted based on the total number of samples falling in each increment. From this figure, it would appear that there exists a certain area in the three-component field representing rocks most likely to expand. The variations in frequency of occurrence of the expanding rocks, which occur in the area between the field of maximum value and the corners for pure calcite and pure dolomite, may or may not be real. Lack of a sufficient number of samples or the use of too fine a grid may be responsible for this apparent anomaly.

SUMMARY

This paper presents the results of various tests on carbonate rock samples taken during a survey of carbonate aggregate sources in Virginia. It was made to determine the carbonate rock types produced in Virginia, the distribution of these rock types, and the possible extent of the problem of alkali reactivity. Based on the results of prism tests in which only 20 samples expanded greater than 0.2 percent at 6 mo, it appears that alkali-carbonate reaction is at present a problem of limited rather than major proportions in Virginia. However, the occurrence of rocks that expand as much as 6.5 percent in the prism test and greater than 0.1 percent in concrete indicates that in specific areas the problem is such as to cause concern.

The composition of reactive-carbonate aggregates from Virginia appears, from the limited data presented, to exhibit certain clearly defined trends. Intermediate calcite and dolomite percentages in the carbonate fraction and high insoluble residue contents are characteristic. From the standpoint of stratigraphy, the reactive samples were concentrated in three formations, Beekmantown, Edinburg and Lowville, all of Ordovician age.

ACKNOWLEDGMENTS

This project was conducted in cooperation with the Bureau of Public Roads and is financed under Highway Planning Research Funds. The financial support, as well as the willing cooperation and suggestions offered by the members of the Physical Research Branch, is appreciated. The authors also wish to extend thanks to Michael Ozol of the Virginia Council of Highway Investigation and Research for aid during the laboratory phases of this work.

The project was under the general direction of Tilton E. Shelburne, Director of Research.

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General Discussion

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•AN INVESTIGATION has recently been completed (1) at the Waterways Experiment Station which indicates that in concrete cores taken from a dam on the Tennessee River near Chattanooga there has been alkali-carbonate rock reaction involving dedolomitization. The carbonate rock aggregate involved in this reaction was obtained from a quarry in the Chickamauga limestone formation. This is believed to represent the first evidence of the occurrence of alkali-carbonate rock reaction in this general geographical area. However, this particular rock has previously been reported to show unusual volume change on wetting and drying (2).

The Chickamauga "formation" includes several formations that have been studied in Virginia and found to contain beds susceptible to carbonate-rock reaction. These formations include the Edinburgh (Athens), the Lincolnshire (Lenoir), and the Newmarket (Mosheim).

REFERENCES

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Part IV.   ANNOTATED BIBLIOGRAPHY

Alkali Reactivity of Carbonate Rocks

DAVID W. HADLEY
Research Geologist, Applied Research Section, Portland Cement Association

1945

WOODS, K. B., SWEET, H. S. and SHELBURNE, T. E. "Pavement Blowups Correlated with Source of Coarse Aggregate." Proc. HRB, 25: 147-168 (1945).

Conclusions: (1) an outstanding correlation existed between certain coarse aggregates used in the concrete mix and the blowup performance of the pavements; (2) no correlation existed between the cement, fine aggregate, traffic or subgrade soils used and blowup performance; (3) extensive laboratory research is necessary to determine the basic reason for variation in performance between aggregate sources and to develop new and better test methods by which those aggregates which produce concrete of an unsatisfactory quality can be identified before they are incorporated in the concrete pavement.

1948

SWEET, H. S. "Research on Concrete Durability as Affected by Coarse Aggregate." Proc. ASTM, 48: 988-1016 (1948).

Extensive field surveys in Indiana showed a correspondence between certain types of pavement disintegration and the source of coarse aggregate. The physical properties of 16 representative aggregates were determined and the performance of these aggregates in laboratory freeze-thaw tests studied. Those aggregates with poor field service records also performed poorly in freeze-thaw tests.

1949

SLATE, F. O. "Chemical Reactions of Indiana Aggregates in Disintegration of Concrete." Proc. ASTM, 49: 954-961 (1949).

Previous field work had shown a correspondence between certain types of disintegration and the source of the coarse aggregate. For the aggregates studied, no appreciable chemical reaction was found that would cause disintegration of concrete.

Sponsored by Committee on Performance of Concrete—Chemical Aspects.

1954

PATTON, J. B. "Petrology of Laminated Limestones in Indiana." Roads and Streets, 97: 8, 85, (Aug. 1954).

Petrographic studies showed many poorly performing carbonate aggregates to have similar lithologies. The poor service record of these aggregates was attributed to their susceptibility to freezing and thawing.

1955

LEWIS, D. W. "Deterioration of Structural Concrete in Indiana." Proc. 41st Ann. Purdue Road School, Ext. Series 88, 39: 5, 97-114 (1955).

Deterioration of a bridge was attributed to chemical reactivity of carbonate coarse aggregate.

ROY, C. J., THOMAS, L. A., WEISSMAN, R., and SCHNEIDER, R. "Geologic Factors Related to Quality of Limestone Aggregates." Proc. HRB, 34:400-411 (1955).

Correlation of petrographic characteristics with service records gave no explanation for the poor service record of carbonate rocks at LeGrand, Iowa. The study of concrete cores indicated that fresh stone gave satisfactory service, whereas weathered stone produced distress. Increased absorption and other effects of weathering produced distress by permitting reactions between cement and aggregates.

1957

BISQUE, R. E. "Limestone Aggregate as a Possible Source of Chemically Reactive Substances in Concrete." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1957).

Limestone from five Iowa quarries was studied by chemical methods as part of a project to determine criteria to differentiate between potentially good and poor concrete aggregates.

RUSH, F. E. "Petrography and Physical Properties of Some Devonian Limestone of Iowa." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1957).

Limestone from two quarries in eastern Iowa, one with a proven undesirable service record as aggregate for concrete highway construction and the other with an apparent acceptable service record, were compared on the basis of porosity, bulk and powder specific gravity, calcite-dolomite ratios, insoluble residue, clay mineralogy and detailed megascopic and microscopic descriptions.

SWENSON, E. G. "A Reactive Aggregate Undetected by ASTM Tests." ASTM Bull. 226, pp. 48-51 (with dis.) (TP236-TP239) (Dec. 1957); HRB Abs., 28: 4, 29 (Apr. 1958).

A Canadian dolomitic limestone coarse aggregate has been found that produces excessive expansion and cracking in concrete. The rate and degree of expansion increased with increasing alkali content of the cement. Pozzolans and chemical admixtures, usually effective in controlling alkali-aggregate reaction, showed somewhat limited beneficial influence. The results of ASTM Test Method C 289 on the limestone were negative. The results of the ASTM mortar bar test were also negative but indicated some alkali-reactivity in the limestone.

1958

BISQUE, R. E., and LEMISH, J. "Chemical Characteristics of Some Carbonate Aggregates as Related to the Durability of Concrete." HRB Bull. 196, pp. 29-45 (1958).

In a study of rocks from several quarries in north-eastern Iowa, certain carbonate rocks developed marked reaction rims in concrete. These rims were not merely a staining phenomenon but represented an increase in silica in the rim zone. The rocks developing rims contained clay, a high percentage of acid insoluble residue, and a high magnesium content.

HILTROP, C. L. "Relation of Pore Size Distribution to the Petrography of Some Carbonate Rocks." Unpubl. M.S. Thesis, Iowa State College (1958).

The pore size distribution curves for the carbonate rocks from five quarries in eastern Iowa were obtained by application of Ruska's mercury injection capillary pressure apparatus. Those rocks were then classified on the basis of their pore size distributions. The relationships between pore size distribution and textural properties, some chemical and physical properties, freeze-thaw results and service record as aggregate for concrete highway were investigated statistically. As is apparent from the scope of this study, the conclusions cannot be extrapolated to encompass all carbonate rocks. Knowledge of pore size distribution might be helpful in predicting service record as concrete aggregate. Further sampling and investigations are necessary to test that possibility.

LEMISH, J., RUSH, F. E., and HILTROP, C. L. "Relationship of Physical Properties of Some Iowa Aggregates to Durability of Concrete." HRB Bull. 196, pp. 1-16 (1958).

A petrographic study was made of carbonate rocks having a poor service record as concrete aggregate and developing reaction rims in concrete. The insoluble residue, clay mineralogy, porosity and pore size distribution were determined. The reaction rims indicated a chemical reaction with the cement that was believed to weaken the concrete and condition it to later failure by freezing or external stresses.

1959

BISQUE, R. E. "Silicification of Argillaceous Carbonate Rocks." Doctoral dissertation, Iowa State College (1959).

A study was undertaken to determine and define the nature of the chemical activity which results in the growth of "reaction shells" in certain carbonate rocks used as coarse aggregate in concrete. The formation of these shells is shown to be due to stabilization of silica from some outside source, in this case the cement paste. Similar reaction shells were grown in aqueous solution under controlled conditions. Only argillaceous carbonate rocks are host to this type of silicification, because the clay material functions as a site of stabilization for silica. The type of chemical activity involved in the growth of these shells is deleterious to the stability of cement paste and distinct from the alkali-aggregate reaction.

BISQUE, R. E., and LEMISH, J. "Insoluble Residue-Magnesium Content Relationship of Carbonate Rocks from the Devonian Cedar Valley Formation." Jour. Sed. Petrol. 29: 1, 73-76 (1959).

The insoluble residue content of carbonate rocks from several quarries in the Devonian Cedar Valley Formation of Eastern Iowa is related to the magnesium content. The relationship of "soluble iron" content to magnesium content is plotted to demonstrate that a high soluble iron content is found only in rocks with a high magnesium content.

HILTROP, C. L., and LEMISH, J. "Treatment of Carbonate Rocks with a Vaporous Mixture of $(CH_3)_2SiCl_2$ and CH_3SiCl_3." Proc. Iowa Acad. of Sci., 66: 214-221 (1959).

Preliminary investigations of the treatment of dry carbonate rocks with some derivatives of silane in the vapor state are described. The treated rocks appear similar to affected aggregates observed in some inferior concretes.

HILTROP, CARL L. and LEMISH, J. "Relationship of Pore-Size Distribution and Other Rock Properties to Serviceability of Some Carbonate Aggregates." HRB Bull. 239, pp. 1-23 (1959).

Rock properties which might affect concrete durability were investigated. Properties studied were effective porosity, total porosity, calcium-to-magnesium ratio, insoluble residue, amount of clay present, freeze-thaw loss, and texture.

LEMISH, J., and BISQUE, R. E. "Autoclave Method for Determining Susceptibility of Carbonate Aggregates to Silicification." Proc., Iowa Acad. of Sci., 66: 210-213 (1959).

Autoclave treatment of concrete bars made from argillaceous dolomitic carbonate aggregates at 420 ± 3 F and 295 ± 10 lb steam pressure for 3 to 9 hr caused the progressive development of silicified reaction shells on the coarse carbonate aggregate similar to those found in distressed concrete. Similar treatment of concrete bars made from pure limestone aggregates induced no reaction shell growth. The susceptibility of carbonate aggregates to silicification could be rapidly determined by the autoclave method.

1960

BISQUE, R. E., and LEMISH, J. "Silicification of Carbonate Aggregates in Concrete." HRB Bull. 239, pp. 41-55 (1960).

Reaction rims were experimentally "grown" by exposing aggregate particles to dilute solutions of sodium silicate or by placing them in mortar bars. The rim zones were more acid resistant than the surrounding rock and were believed due to the introduction of silica from the cement paste. The development of rims may represent a deleterious form of silica activity, distinct from the alkali aggregate reaction.

BISQUE, R. E., and LEMISH, J. "Effect of Illitic Clay on Chemical Stability of Carbonate Aggregates." HRB Bull. 275, pp. 32-38 (1960).

Reaction rims may be the result of polymerization of soluble silica on the surfaces of illitic clay particles within rock, causing formation of a three-dimensional network of clay particles "tied together" with stabilized silica. The development of compressive strength was diminished when rim development occurred in concrete subjected to a wetting and drying-heating and cooling cycle.

HARWOOD, R. J. "Compositional Variations Associated with Carbonate Aggregate-Cement Paste Reactions." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1960).

Cubes of various types of carbonate rocks were placed in bars of cement paste or alite. After 3 mo in hot distilled water, samples, taken at specified distances from the cement-aggregate interface, were analyzed chemically. Depending on the character of the aggregate, silica moved either in or out of the interface zone of the aggregate, calcium generally moved in, and magnesium could move in either direction.

HILTROP, C. L. "Silica Behavior in Aggregates and Concrete." Doctoral dissertation, Iowa State Univ., Ames, Iowa (1960).

To study the mobility and direction of movement of silicate ion in the development of reaction rims, samples of two carbonate rocks and three cements were refluxed in distilled water for 48 hr. Reaction rims were formed in a few days. Carbonate rocks were also treated with tetrachlorosilane vapor.

SWENSON, E. G. and GILLOTT, J. E. "Characteristics of Kingston Carbonate Rock Reaction." HRB Bull. 275, pp. 18-31 (1960).

The excessive expansion and cracking of concretes with argillaceous dolomitic limestones from Kingston, Ontario, used as aggregate may be due to a chemical reaction different from other previously described cement-aggregate reactions. Although standard ASTM methods of test for potential alkali-aggregate reactivity do not reveal the reactive tendencies of the aggregate, they may be detected by measuring the expansion of concrete prisms in a highly humid atmosphere. The variables influencing the expansion of affected concrete are discussed. A possible relationship between expansive reactivity and the reaction of dolomite with the cement alkalies is suggested. The use of cement with sufficiently low alkali content appears to have provided a satisfactory solution to the field problem in the Kingston area.

SWENSON, E. G. and LEGGET, R. F. "Kingston Study of Cement-Aggregate Reaction." Can. Cons. Eng., 2: 8 (Aug. 1960); Tech. Paper 103, Div. of Building Res., Nat. Research Council, Canada (NRC 5904).

The effect of alkali-carbonate reactivity on field concrete in the Kingston, Ontario, area is described. Laboratory studies are summarized and the construction practices believed best suited for concretes made with potentially reactive aggregates are listed.

1961

FELDMAN, R. F., and SEREDA, P. J. "Characteristics of Sorption and Expansion Isotherms of Reactive Limestone Aggregate." Jour. Amer. Conc. Inst., Proc., 58: 2, 203-214 (Aug. 1961).

Characteristic differences have been detected in the sorption and expansion isotherms of alkali-treated and untreated reactive limestone aggregate. These results are compared with those obtained from Vycor glass under similar conditions. The evidence establishes the presence, within the pores of the aggregate, of trace amounts of a material that causes expansion when water is made available to it. The mechanism of expansion is similar to the alkali-silica complex formed in the pores of Vycor glass although the composition of the materials in the two cases may be different.

HADLEY, D. W. "Alkali Reactivity of Carbonate Rocks — Expansion and Dedolomitization." Proc. HRB, 40: 462-474 (1961); PCA R&DL Bull. 139.

The reactive rocks expanded rapidly in concrete and in highly alkaline solutions. This expansion accompanied the chemical reaction $CaMg(CO_3)_2 + 2MOH \rightarrow M_2CO_3 + Mg(OH)_2 + CaCO_3$, in which M = K, Na, or Li. The reactive rocks were categorized by mineral composition and texture, and a simple and rapid laboratory test for the expansive reaction in alkali was described.

LEGGET, ROBERT F., and GIBBONS, E. V. "Concrete Durability Studies in Canada." RILEM Intern. Sym. on Durability of Concrete, Final Rep., Prague, 2: 303-310 (1961).

Studies are outlined which have contributed in making concrete durable to Canadian conditions of exposure. Reference is made to the work done in developing a sulfate-resisting type of cement, a basis for classifying deleterious characteristics of aggregates, and improved resistance to de-icing salts. Concrete failures due to alkali-aggregate reaction are briefly described with special mention of an unusual type involving a dolomitic limestone.

LEMISH, JOHN "Research on Carbonate Aggregate Reactions in Concrete." Trans. AIME, 220, pp. 195-198 (1961).

Distress in concrete related to carbonate aggregates is widely recognized. It generally occurs after 15 yr of service. The matrix is highly carbonated and dark borders or reaction shells outline the argillaceous carbonate aggregate fragments. Controlled laboratory experiments show that all components of the rock react to form a silicified dedolomitized shell. Na and K are not introduced into the shell which represents the presence of amorphous silica derived mostly from quartz in the rock. The silica is absorbed or fixed by the aggregate as a hydrated Ca silicate compound. Concrete in which the reaction has occurred does not gain in strength. Concrete bars unaffected by the reaction increased 50% in strength.

WERNER, M. A. "Equilibria in Cement Paste-Carbonate Aggregate Reactions." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1961).

Selected rocks and cements were placed in contact with solutions of various silicon concentrations and refluxed for 48 hr. The solutions were then analyzed for calcium, magnesium, and silicon. A definite silicon equilibrium existed between the rock and the aqueous solution.

1962

BISQUE, RAMON E. "Clay Polymerization in Carbonate Rocks: A Silicification Reaction Defined." Nat. Conf. on Clays and Clay Minerals, 9th Proc., 9: 365-373 (1962).

A carbonate rock silicification reaction was defined and shown to be dependent on the presence of clay in the host rock. Introduction of silica in soluble form(s) serves to polymerize the clay fraction, forming three-dimensional network which can be separated from the rock by leaching away the carbonate minerals. Laboratory silicification of argillaceous carbonate rocks under controlled conditions has served to define critical variables.

DE GAST, A. A. "The Study of the Physical Properties of Kingston Limestone Deleterious in Concrete." Unpubl. M.S. Thesis, Queen's Univ. (1962).

The role of the release of residual strain in the rock in observed expansion of concretes containing Kingston aggregate is studied and shown not to be significant factor.

LEMISH, J. Discussion of "Chemical Reactions Involving Aggregates," by Per Bredsdorff, G. M. Idorn, A. Kjaer, N. M. Plum and E. Poulsen. Intern. Sym. on Chemistry of Cement, 4th Proc., Washington, 2: 296-299 (1960); U. S. Dept. of Commerce NBS Mono. 43 (1962).

Research at Iowa State University has shown that cement-aggregate reaction is selective and that dolomitic argillaceous carbonate rocks characterized by relatively high residues react with cement. All components of the rock react to form a silicified "dedolomitized" shell. Silica can move either into or out of an aggregate.

MATHER, KATHARINE, and BUCK, ALAN D. "Alkali-Silica and Alkali-Carbonate Reactivity of a South Dakota Sand." U. S. Army Engineers Waterways Exp. Station, Misc. Paper 6-53 (Sept. 1962).

Studies of mortar bars and samples of two sands from Watertown, S. D., area at the Waterways Experiment Station revealed (a) alkali-aggregate reaction of the shale particles involving low cristobalite-tridymite, a form of silica present in the shale; (b) concurrent cation exchange involving the montmorillonite; (c) alkali-aggregate reaction involving carbonate rock particles, i. e., dedolomitization in which brucite is a reaction product. This represents the first evidence of alkali-carbonate rock reaction, dedolomitization, recorded by the Corps of Engineers.

NEWLON, H. H., Jr., and SHERWOOD, W. C. "Potentially Reactive Carbonate Rocks." Proc., 21st Meeting Southeastern Assoc. of State Highway Officials (1962).

This paper includes preliminary findings of a statewide survey of Virginia carbonate aggregate sources. Rock from seven quarries was found to expand more than 0.2% in the rock prism expansion test. This was the minimum rock expansion found to produce distress in laboratory concrete. Extensive laboratory studies are described.

NEWLON, H. H., Jr., and SHERWOOD, W. C. "An Occurrence of Alkali-Reactive Carbonate Rock in Virginia." HRB Bull. 355, pp. 27-44 (1962).

A highway bridge in Virginia, which had been instrumented to measure concrete shrinkage, was found instead to undergo a progressive expansion of considerable magnitude. The carbonate coarse aggregate was subsequently determined to be alkali-reactive. Extensive laboratory tests of the aggregate largely confirmed the published findings of earlier investigations.

WALLACE, C. M. "Relationship of Pore Size to Texture in Some Carbonate Rocks." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1962).

The effective porosity was determined for six different carbonate rocks from five Iowa quarries. A thorough knowledge of a rock's effective porosity, volume/surface ratio, and chemical composition may be helpful in predicting the suitability of the rock as a concrete aggregate.

1963

GILLOTT, J. E. "Petrology of Dolomitic Limestones, Kingston, Ontario, Canada." Geol. Soc. Amer. Bull., 74: 6, 759-778 (June 1963).

Dolomitic limestone from Kingston, Ontario, has importance as an example of rock which produces in concrete an alkali-aggregate reaction different from reported alkali-silica reaction. The expansive reaction causes deterioration and cracking of the concrete. A petrographic, mineralogical, and chemical comparison was made between rock showing high expansion in concrete and no reactivity. Although it is not possible on petrographic criteria alone to predict the degree of reactivity which a particular rock may show as aggregate, rocks of this petrographic type may be recognized.

LEMISH, J. "Carbonate Aggregate Research." Proc., 14th Ann. Highway Geology Sym., Texas A and M College, pp. 55-64 (1963).

Research concerning the reactivity of carbonate aggregates is reviewed. No one mechanism or variety of mechanisms for the contribution of carbonate rocks to distress in concrete can be postulated at this time.

LEMISH, J., HARWOOD, R. J., HILTROP, C. L., and WERNER, M. A. "Compositional Variations Associated with Carbonate Aggregate Reactions." Highway Res. Record 3, pp. 1-8 (1963).

Changes in the composition of aggregates and cement pastes were studied by placing cubes of various aggregates in cement paste bars and reacting them in a water bath at 130 F for 3 mo. The silica in the shell zone is locally derived from quartz present in the aggregate and migrates in the direction required to maintain equilibrium at the pH present. Dedolomitization and possibly an increase in new calcite occurs concurrently. Cement pastes are stable and are not considered the source of silica found in the shell zone.

MATHER, K., LUKE, W. I., and MATHER, B. "Aggregate Investigations, Milford Dam, Kansas, Examination of Cores from Concrete Structures." U. S. Army Engineers Waterways Exp. Station, Tech. Rep. 6-629 (June 1963).

Cores from Kansas and Nebraska containing several sand-gravel and crushed limestone-sand gravel combinations were studied using petrographic and X-ray test methods. Both alkali-silica and alkali-carbonate reactions were found in most of the concretes examined. Reaction rims developed on some non-dolomitic aggregate particles.

MOORE, W. J. "Studies of Carbonate Aggregate Reactions: Expansion Behavior; Environmental Effects; Concrete Matrix Investigations." Unpubl. M.S. Thesis, Iowa State Univ., Ames, Iowa (1963).

Studies of the expansive behavior of reactive dolomitic limestones from Iowa largely confirmed the findings of earlier investigators. Appreciable expansion took place only in those rocks with an initial effective porosity of less than 8%. Results of research concerning the development of reaction rims in the laboratory are given, and preliminary studies of variations with depth in the chemical composition of cement paste separated from highway cores are described.

NEWLON, H. H., Jr., and SHERWOOD, W. C. Discussion of "Durability of Concrete in Service," Jour. ACI Proc., 60: 6, Pt. 2, 2071-2075 (June 1963).

Preliminary results are presented of a survey of carbonate rocks from all commercial sources in Virginia. A total of 284 samples were tested in the rock prism expansion test. Expansions of up to 2.85% were measured after 10-mo soaking in 1 M NaOH.

1964

AXON, E. O., and LIND, J. "Alkali Carbonate Reactivity — An Academic or a Practical Problem." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Although no serious reduction in the service life of the concretes on Missouri highways has been attributed to alkali reactive aggregates, results of the rock prism expansion test on more than 230 samples indicated that some rocks in Missouri were sufficiently reactive to cause concern.

DOLAR-MANTUANI, L. "Expansion of Gull River Carbonate Rocks in Sodium Hydroxide." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

The rocks of this formation were sampled over a broad area and tested in the rock prism expansion test. Certain of the reactive rocks were found to expand only after extended soaking in alkaline solution.

GILLOTT, J. E. "Study of Alkali Carbonate Rock Reactivity by a Cell Test Method." Paper submitted to ASTM.

GILLOTT, J. E. "Mechanism and Kinetics of Expansion in the Alkali-Carbonate Rock Reaction." Paper submitted to Geol. Soc. Amer.

HADLEY, D. W. "Alkali Reactivity of the Dolomitic Carbonate Rocks." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

The performance of the alkali-reactive carbonate rocks in field and laboratory concretes is described, and published and unpublished research concerning the causes and mechanisms of reactivity is reviewed and discussed. Known occurrences of potentially reactive rocks are noted, rapid laboratory tests for the recognition of the reactive rocks are summarized, and various remedial measures are discussed.

HADLEY, D. W. "Alkali Reactive Carbonate Rocks in Indiana—A Pilot Regional Investigation." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

A study of the carbonate rocks exposed in Indiana showed that by utilizing standard geologic field techniques coupled with specially developed but simple and rapid laboratory tests, the distribution of the reactive rocks within the vertical sequence of beds and the geographic areas in which these reactive rocks were exposed could be rapidly delineated. The reactive rocks were widely distributed in Indiana. Fortunately, however, the reactive beds are normally thin, the general level of reactivity is low and most of the highly reactive materials are of poor physical quality and consequently are not used as concrete aggregate. Studies on laboratory concretes indicate that many of the marginally reactive materials could be safely used as concrete aggregate if adequate precautions were taken.

LEGG, F. E., Jr., and VOGLER, R. H. "Alkali-Carbonate Rock Reactions in Michigan." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Laboratory studies have disclosed three quarried limestones having very mild expansions when incorporated in concrete made with high-alkali cement. The freeze-thaw durability of two of these limestones is dependent upon the alkali content of the cement when the aggregates are placed in the concrete in a vacuum saturated condition. Durability was improved with low alkali cement. The Michigan State Highway Department has not experienced distress of field concrete positively identified as being due to cement alkali-carbonate rock reaction.

LEMISH, J., and MOORE, W. J. "Carbonate Aggregate Reactions: Recent Studies and an Approach to the Problem." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Expansion studies were made on a variety of carbonate rocks occurring in Iowa. Results reported favored a causative mechanism of expansion most closely related to rock texture and pore structure. The results of comparative studies on laboratory methods for inducing the development of reaction rims were given, and an approach to the problem of deleterious behavior of certain varieties of carbonate rocks in concrete through a systematic study of highway concrete was described.

MATHER, K., BUCK, A. D., and LUKE, W. I. "Alkali-Silica and Alkali-Carbonate Reactivity of Some Aggregates from Kansas, South Dakota, and Missouri." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Results of the detailed petrographic examination of concretes showing alkali-silica and/or alkali-carbonate reactions are presented.

NEWLON, H. H., Jr., and SHERWOOD, W. C. "A Study of Remedial Methods for Reducing Alkali-Carbonate Reaction." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Dilution with non-reactive aggregate and the use of low alkali cement were investigated as possible remedial measures for alkali-carbonate reactivity. The most important influence on the expansion of concrete affected by the alkali-carbonate rock reaction was the level of aggregate reactivity. Dilution with inert aggregate appeared to be a better procedure than limitation of cement alkalies.

SHERWOOD, W. C., and NEWLON, H. H., Jr. "Studies on the Mechanisms of Alkali-Carbonate Rock Reaction." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Results are reported of laboratory studies made to determine the chemical reactions that may contribute to the expansion of concrete made with the alkali-reactive carbonate rocks. The major mineral constituents of the reactive rocks were studied before and after treatment with alkaline solutions, and the evidences of reaction noted during this phase of the study were then looked for in thin sections, prisms, and in aggregate from laboratory and field concrete.

SHERWOOD, W. C., and NEWLON, H. H., Jr. "Statewide Survey for Reactive Carbonate Aggregates in Virginia." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Carbonate aggregate sources in Virginia were systematically sampled and the rock tested for expansion in alkali and for development of reaction rims in concrete.

SMITH, P. "Learning to Live with a Reactive Carbonate Rock." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

An investigation was made to determine the safest and most economical way of building a four-lane concrete highway for 30 mi west of Kingston, Ontario, where the local dolomitic limestone aggregates might show expansive reactivity in concrete. Aggregates were ultimately selected on the basis of the expansion of concretes made with cement high in alkalies and cured under standard conditions. The precautions taken to insure that only non-reactive aggregates were used and the other factors favoring minimized expansion are described.

SWENSON, E. G., and GILLOTT, J. E. "Alkali-Reactive Carbonate Rock — NRC Canada Studies." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

A review is made of 8 yr of published research on the alkali-carbonate rock reaction by the Division of Building Research, National Research Council, Ottawa, Canada. The Kingston case which first revealed excessive expansion in concrete by alkali-carbonate reactivity in a dolomitic limestone coarse aggregate is summarized. Further field studies are described as well as investigations into the nature of the reaction, methods of test and identification, and some hypotheses concerning the mechanism of reaction and expansion.

WELP, T. L., and DE YOUNG, C. "Variations in the Performance of Concrete with Carbonate Aggregates in Iowa." Paper presented at 43rd Ann. Meeting HRB (Jan. 1964).

Observation of concrete pavements for several years indicates that the majority of the carbonate aggregates used can be expected to perform satisfactorily for at least 20 to 25 yr. Several aggregates from various geologic sources were used in concrete pavement over 40 yr old. Of over 100 carbonate aggregate sources used, only a few have been associated with early deterioration of concrete. Three known geologic sources capable of meeting current test limits are associated with concrete that has shown extensive deterioration on pavements from 8 to 15 yr old. These three are in different stratigraphic horizons with different lithologies, but have no distinction properties that separate them from acceptable geologic sources. Carbonate content is 95% or more.