



NRC Publications Archive Archives des publications du CNRC

Characteristics of Kingston carbonate rock reaction

Swenson, E. G.; Gillott, J. E.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Highway Research Board Bulletin, 275, pp. 18-31, 1961-08-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=c6df3ea9-34f8-40de-b506-fe7aab0401ba>
<https://publications-cnrc.canada.ca/fra/voir/objet/?id=c6df3ea9-34f8-40de-b506-fe7aab0401ba>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



Ser
TH1
N21r2
no. 130
c. 2

~~BLDG~~

NATIONAL RESEARCH COUNCIL
CANADA

ANALYZED

DIVISION OF BUILDING RESEARCH

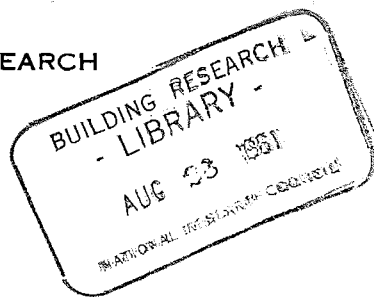
CHARACTERISTICS OF KINGSTON CARBONATE ROCK REACTION

BY

E. G. SWENSON AND J. E. GILLOTT

REPRINTED FROM
HIGHWAY RESEARCH BOARD BULLETIN NO. 275, 1960,
P. 18 - 31

RESEARCH PAPER NO. 130
OF THE
DIVISION OF BUILDING RESEARCH



OTTAWA

AUGUST 1961

PRICE 25 CENTS

NRC 5583

5225

This publication is being distributed by the Division of Building Research of the National Research Council. It should not be reproduced in whole or in part, without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division of Building Research may be obtained by mailing the appropriate remittance, (a Bank, Express, or Post Office Money Order or a cheque made payable at par in Ottawa, to the Receiver General of Canada, credit National Research Council) to the National Research Council, Ottawa. Stamps are not acceptable.

A coupon system has been introduced to make payments for publications relatively simple. Coupons are available in denominations of 5, 25 and 50 cents, and may be obtained by making a remittance as indicated above. These coupons may be used for the purchase of all National Research Council publications including specifications of the Canadian Government Specifications Board.

CISTI/ICIST



3 1809 00210 9392

ANALYZED

Characteristics of Kingston Carbonate Rock Reaction

by

E. G. SWENSON and J. E. GILLOTT
Research Officers, Building Materials Section
Division of Building Research
National Research Council, Ottawa, Canada

Reprinted from Bulletin 275 (1960)
Highway Research Board, Washington, D.C., USA

NRC 5583

3358153

Characteristics of Kingston Carbonate Rock Reaction

E. G. SWENSON*, and J. E. GILLOTT, Research Officers, Building Materials Section, Division of Building Research, National Research Council, Ottawa, Canada

● THE EXCESSIVE expansion and cracking of concrete in which argillaceous dolomitic limestones from Kingston, Ontario are used as aggregates, has certain unusual features when compared with the effects of alkali-silica reactivity normally associated with alkali-aggregate reaction. Since the publication of preliminary studies of this case (1), further research in this laboratory, together with reports of another apparently related phenomenon (2, 3) has indicated that the mechanism of this reaction may possibly be different from other previously described cement-aggregate reactions.

The use of cement with sufficiently low alkali content appears to have provided a satisfactory solution to the field problem in the Kingston area. Although standard ASTM methods of test for potential alkali-aggregate reactivity failed to reveal this behavior, it may be detected by measuring expansion of concrete prisms exposed to a highly humid atmosphere (1).

In this paper laboratory results are presented that show the marked differences and similarities between the characteristics of this phenomenon and those of the well-known alkali-silica reaction. Much of the data were obtained on concrete test specimens and are, therefore, considered to be of practical value also.

GENERAL MANIFESTATIONS OF THE REACTION

The phenomenon is characterized by excessive expansion and cracking of concrete when a high alkali cement is used and the concrete is exposed to a moist environment. In sidewalks and floor slabs, where the bottom side is exposed to a continuously humid atmosphere and the top side is exposed to the weather, differential movement has produced a characteristic pattern cracking (Fig. 1). In the field these cracks penetrate about two-thirds of the depth of an average slab. The areas surrounded by the cracks, from 2 to 4 in. across, appear to be relatively sound. Spalling does not appear to be characteristic of this reaction and edges at the cracks are still sharp in cases more than 20 years old. There is no megascopic evidence on the surface or in the cracks of old or new affected concretes of any material or formations that are foreign to normal concrete.

Great variability in both rate and degree of expansion and cracking has occurred in field concrete where Kingston carbonate rock has been used as coarse aggregate. In laboratory concrete, kept continuously in the curing chamber, expansion has reached 0.1 percent within six weeks. Cracking occurs at expansions of about 0.05 to 0.10 percent. In extreme cases in the field, cracking has occurred within two to three months of placing.

Using the same reactive aggregate and a cement with low alkali content, no excessive expansion has occurred to date in laboratory concretes after nearly 4 years in a highly humid environment and in field concrete after two years exposure.

RESPONSE OF VARIOUS METHODS OF TEST

The failure of the standard ASTM test methods to show potential deleterious alkali-reactivity in the Kingston carbonate rock has been previously reported (1). Consider-

*Now with Miron Freres, Montreal.

able additional work with these tests and certain modifications of them confirmed the earlier findings.

Mortar Bar Test

In the mortar bar test (ASTM Designation C227-52T) the Kingston rock produced abnormal expansion but, on the basis of accepted criteria for alkali-silica reactivity (0.05 percent at 3 months and 0.10 percent at 6 months), this rock would be classified as not deleteriously reactive to cement alkalis. Typical expansions at 3 and 6 months are given in Table 1 for the "very reactive" and the "least reactive" from each of two major quarries. Expansions of the concrete prisms, in which the rock is in the form of coarse aggregate (maximum size, $\frac{3}{4}$ in.) are much greater in both rate and degree. It should be noted that the mortar bars are conditioned at 100 F whereas the concrete prisms were conditioned at 73 F and 100 percent relative humidity. The low expansions of both mortar bars and concrete prisms are of the same order when a low alkali cement is used.

Mortar bars containing very reactive aggregate were continued in the test and at the end of 39 months showed an expansion of 0.060 percent. The corresponding bars made with the low alkali cement had expanded 0.035 percent at this age. Rate and degree of expansion of the mortar bars were not reduced when a lower water-cement ratio was used. In this respect the phenomenon differs from the alkali-silica type. The very active calcined shale, when substituted for 25 percent by weight of the cement, reduced expansion in the mortar bar test by about the same amount as the low alkali cement (1). It is clear that the mortar bar test will give an indication of this phenomenon but a different criterion would have to be established from that used for alkali-silica type reactions.

Quick Chemical Test

The quick chemical test (ASTM Designation C289-54T) was found to be inapplicable as a method for detecting the adverse behavior of the Kingston dolomitic limestone (1). The average silica release for the most reactive rock was 18.4 millimoles per liter; average reduction in alkalinity was 144 millimoles per liter. These values would lead one to conclude that the aggregate is free from deleterious alkali-reactivity. The corresponding values for the least reactive rocks were 8.3 and 323 millimoles per liter. The inadequacy of the present test where dolomitic limestones are concerned has been noted and possible modifications suggested both in procedure and interpretation (1, 4, 5). One such modified procedure, in which the determinations were made on the acid insoluble residue, gave values of silica release and reduction in alkalinity of 49.1 and 23.6 millimoles per liter, respectively, when recalculation on the basis of the original rock. These values could be interpreted as indicating potentially deleterious alkali-silica reactivity. Similar values were, however, obtained for the "nonreactive" rock.

Conrow Test

In the Conrow test (ASTM Designation C342-55T) the very reactive Kingston rock gave expansions that were not significantly greater than those of nonreactive rocks. At 12 months the values for the very reactive rock when made with high and low alkali cements, were 0.029 and 0.018 percent, respectively. The corresponding values for the "nonreactive" Kingston rocks were 0.029 and 0.040 percent and for the nonreactive control rock, 0.012 and 0.021 percent.

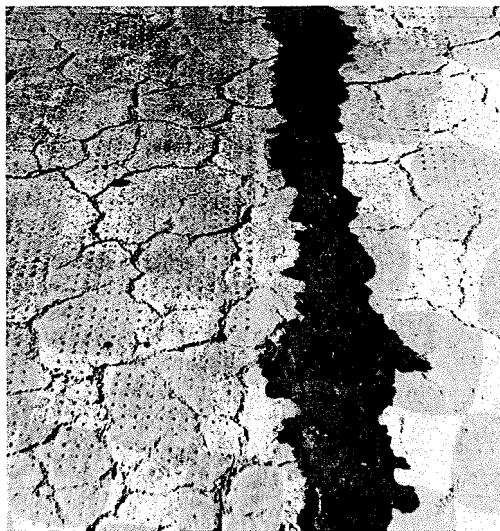


Figure 1. Map cracking in a sidewalk in Kingston.

TABLE 1

EXPANSIONS IN STANDARD ASTM MORTAR BAR TEST COMPARED WITH
THOSE OF CONCRETE PRISMS CONDITIONED AT 100 PERCENT
RELATIVE HUMIDITY AND 73 F

Carbonate Rock	Quarry Level (feet)	Percent Cement Alkali, as Na ₂ O	Linear Expansion (percent)			
			3 Months		6 Months	
			Mortar Bar Test	Concrete Prisms	Mortar Bar Test	Concrete Prisms
<u>Quarry A</u>						
Very reactive	0-24	1.19	0.031	0.175	0.043	0.235
Very reactive	0-24	0.45	0.016	0.018	0.024	0.023
Least reactive	24-30	1.19	0.005	0.016	0.006	0.018
<u>Quarry B</u>						
Very reactive	0-12	1.19	0.025	0.063	0.033	0.092
Least reactive	12-13	1.19	0.004	0.021	0.009	0.030
<u>Control</u>						
Nonreactive	-	1.19	0.004	0.003	0.004	0.004

Petrographic Examination

Petrographic examination of cut and polished sections of affected field and laboratory concrete at ages up to 3 years showed that the reaction had some characteristics very similar to the alkali-silica reaction. It lacked certain other features, however, that have been established as essential characteristics of such reactions by study of many such cases. The following observations are based on examinations made by authorities on alkali-aggregate reaction at the request of the authors (6, 7) and on the findings of this laboratory.

Many of the carbonate rock particles exhibit "reaction rims": some are narrow and dark and others are wider and less well-defined. The dominant silica mineral is quartz which is not known to be deleteriously reactive to cement alkali.

Fracturing is abundant and penetrates the carbonate rock particles as well as the cement mortar, but only a very small quantity of alkali silica-gel can be detected. Considerable micro-fracturing was observed and the freshly broken mortar surfaces had a slightly chalky appearance. A significant number of contact surfaces between the cement paste and aggregate particles had been disrupted by large fractures and micro-fractures, and many of the sockets from which the particles were removed showed slight brownish stains. Deposited on the fracture surfaces were varying amounts of calcium carbonate and calcium sulphoaluminate, the latter in somewhat larger amount than normal. There appeared to be some similarity between these affected concretes and concretes that have responded to the Scholer test.

Where low-alkali cements had been used and no excessive expansion had occurred, there was also rim formation, the rims generally being broader and about as prevalent as in affected concretes made with a high-alkali cement.

Concrete Prism Test

The concrete prism test was the only method found to be reliable in detecting the type of alkali-reactivity present in the Kingston dolomitic limestone. It consisted of measuring length change of concrete prisms continuously conditioned at near 100 percent relative humidity and 73 F. The rate and degree of expansion were compared for concretes made with the Kingston limestones and low- and high-alkali cements, and similar control specimens made with nonreactive limestones. The method has the practical advantage of being a direct test on concrete. Careful control permitted detection of reactivity through abnormal expansion after only three or four weeks for

the very reactive rocks, but several months, or even a year or more, may be required for less reactive rock or for evaluating the effectiveness of low-alkali cement in reducing expansion to a safe value.

Expansion of concrete prisms accelerated slightly when subjected to higher temperatures or to a wetting-drying cycling action such as a modified Scholer test (8). The advantage is more than offset, however, by the more complicated apparatus required and the greater difficulty of control. Comparable results of these tests are given later.

The concrete prisms used in these tests were 3- by 4- by 16-in. or 3- by 3- by 10-in., with reference studs inset at each end during fabrication. The moulds were lined with vinyl sheeting to avoid a coating of grease. The comparator (Fig. 2) was so designed that the prism rested on a firm base; the measuring plug at the bottom was adjusted to the measuring stud on the prism by means of a counterweight system. The micrometer at the top measured to the nearest 0.001 in.

Concrete mixtures were all in the range of normal job concretes with control mixtures made at the same time and in exactly the same way as the test mixtures. Cement-sand ratios were 1:2 and 1:2 $\frac{1}{4}$; cement-stone ratios varied from 1:2 $\frac{1}{4}$ to 1:3 $\frac{1}{2}$, depending on the maximum size stone. Water-cement ratios ranged from 0.44 to 0.60 by weight with slumps from $\frac{1}{2}$ in. to 3 in. for all except special cases.

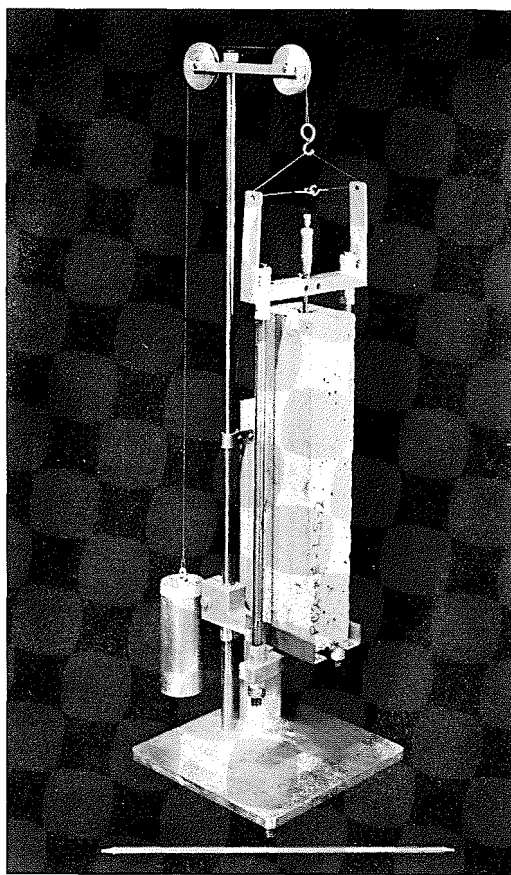


Figure 2. Comparator assembly for measuring length change of concrete prisms.

CHARACTERISTICS OF THE REACTION IN CONCRETE

Influence of Composition

Cement Alkali.—The direct influence of the alkali content of the cement on the abnormal expansion of concretes made with the reactive dolomitic limestone is shown in Figure 3. Concrete mixture proportions were 1:2 $\frac{1}{4}$: 2 $\frac{1}{3}$, with a $\frac{1}{2}$ -in. maximum size stone and a water-cement ratio of 0.47. Each curve represents the average linear change of two 3- by 3- by 10-in. prisms maintained continuously at near 100 percent relative humidity and 73 F. The total percent cement alkali (calculated as sodium oxide) with the sodium and potassium oxide values for each (given in brackets) were: 0.99 (0.96, 0.05); 0.52 (0.46, 0.09); and 0.10 (0.01, 0.14).

Cracking of the affected concretes became visible at expansions of 0.06 to 0.10 percent. The control concrete made with a nonreactive reference limestone and a high-alkali cement showed negligible expansion of the same order as the bottom curve of Figure 3.

The increase in the rate and degree of expansion with increasing alkali content was found to hold whether all the alkali derived from the cement or whether part of the alkali was added. The effect of added alkalis is shown in Figure 4. Mixture proportions were 1:2:3 $\frac{1}{4}$, with a maximum size aggregate of $\frac{3}{4}$ in. and a water-cement ratio of 0.475. The low alkali cement used contained 0.31 percent total alkali calculated as

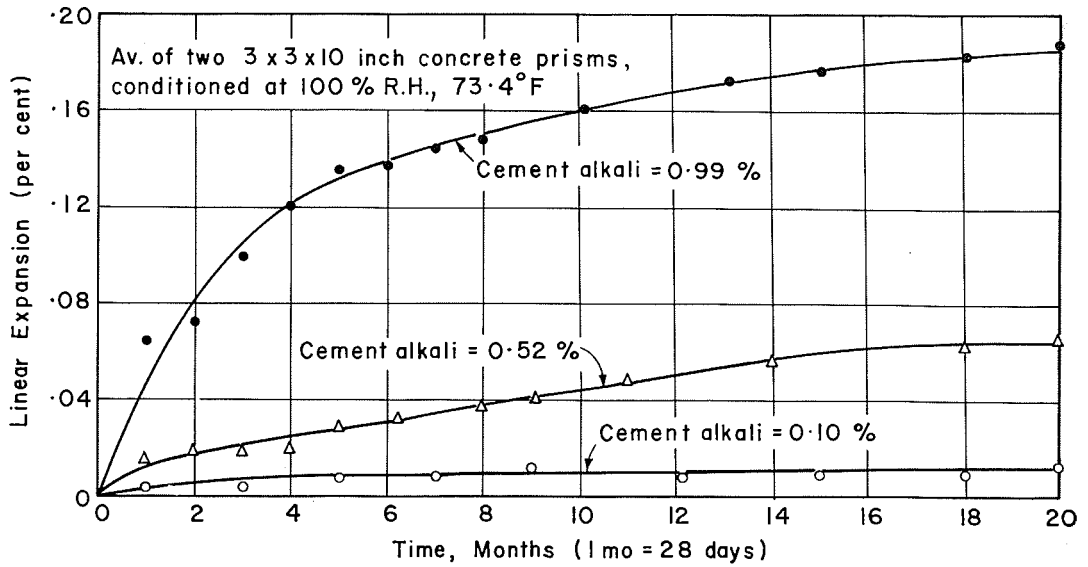


Figure 3. Effect of cement alkali content on expansion of concrete containing reactive Kingston carbonate rock as coarse aggregate.

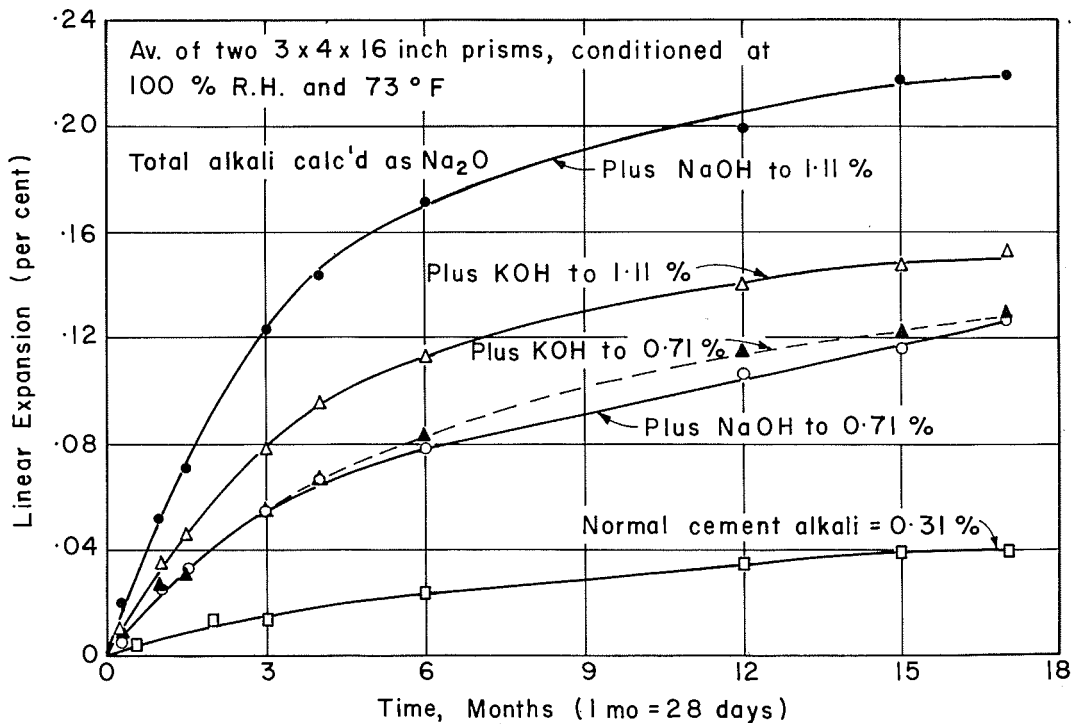


Figure 4. Concrete expansion with reactive carbonate rock and low alkali cement with added alkalis.

sodium oxide (0.14 percent sodium oxide and 0.26 percent potassium oxide). Increments of sodium and potassium hydroxide were added to the mixing water in equimolecular quantities to give total alkali contents of 0.71 and 1.11 percent. The plots are derived from the average expansions of duplicate 3- by 4- by 16-in. prisms conditioned continuously at 100 percent relative humidity and 73 F. Results similar to those in Figure 4 were obtained with a low-alkali Type V cement when sodium hydroxide was added to the mixing water.

With higher alkali contents, the sodium form of the alkali was more aggressive than the potassium form. This characteristic of the reaction is similar to that for the alkali-silica type (9), and was observed in other tests using different cements. These results indicated that the alkali was the only component of the cement that acted as the reactant or catalyst in the reaction of the carbonate rock. This conclusion was supported by expansion results involving a total of 15 cements varying in composition and fineness.

From a practical point of view, these and many other experimental results indicated that the generally accepted limit of 0.6 percent on total cement alkali where an alkali-reactive aggregate is to be used, is too high for the Kingston rock. It is suggested that a limit of 0.45 or 0.40 percent be accepted for this case.

Potential Inhibitors.—Partial replacement of the high-alkali cement with pozzolanic materials, an effective method of inhibiting alkali-silica reactions, appeared to be effective for a limited period but not at later ages for concretes made with the Kingston rock. This is illustrated in Figure 5, where expansions of concretes with no replacement are compared with concretes in which 25 percent of the cement, by weight, was replaced by an active calcined shale and by a fly ash (cement alkali = 1.19 percent, calculated as sodium oxide). This limited influence of a pozzolan does not necessarily indicate a difference in behavior of this reaction from the alkali-silica type; rather it may be due to the degree of reactivity present. Nevertheless, it was found that a 1 percent addition of lithium chloride, an effective inhibitor of alkali-silica reactions (10) had no retarding influence on this reaction at early or at late ages.

Ten pozzolanic materials were tried, some in 25 percent replacement of cement by weight, and others in 25 percent replacement by volume. Some had no effect, others a small early influence, taking into account the reduction in alkali as a consequence of reduction in cement.

It should be remembered that the calcined shale appeared to have a definite inhibiting influence in the mortar bar test.

Aggregate Size.—The rate and degree of expansion of concretes made with the Kingston rock and a high alkali cement were found to decrease with decreasing maximum size of aggregate. This is shown in Figure 6, where the expansion of the concrete made with $\frac{3}{8}$ to $\frac{1}{2}$ -in. rock is greater than that for the concrete made with $\frac{1}{4}$ to $\frac{3}{8}$ -in. rock. The dotted line shows the expansion of the mortar bars made with the rock (maximum size $\frac{1}{4}$ in.).

Other Variables in Concrete.—The rate and degree of expansion of concretes made with the reactive Kingston limestone and a high alkali cement was found not to be significantly influenced by varying the water-cement ratio between 0.44 and 0.70. The lower water-cement ratios actually gave slightly higher expansions both for the cements and the mortar bars. In this respect the reaction differs from the alkali-silica type.

The moisture condition of the aggregate prior to incorporation in the concrete also had no significant influence in the expansion; however, saturated aggregate produced slightly higher expansion than aggregate exposed to laboratory drying or to 100 percent relative humidity conditions.

The type, grading, and proportion of siliceous sand had no detectable influence when used with the reactive-rock coarse aggregate. No measurable increase in expansion was obtained when the siliceous sand was replaced by sand made from the reactive limestone.

Entrained air did not appear to have any influence on the expansion of concretes containing the reactive combinations. Variation in method and degree of compaction and in finishing techniques also had no observable effect.

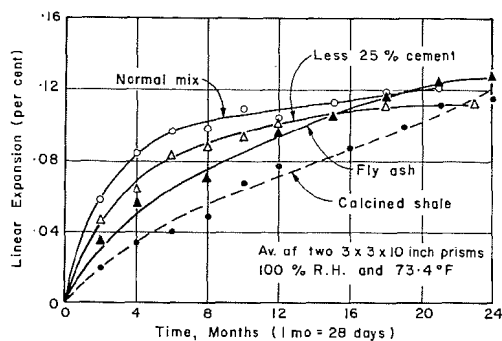


Figure 5. Influence on expansive concrete of reduction in cement and of partial replacement by pozzolans.

The most reactive rock is found in the top 24 ft of Quarry A. It has been used extensively as coarse aggregate for concrete in the Kingston area, and was used in most of the studies of the characteristics of the reaction. Physically it was found to be satisfactory as a coarse aggregate when evaluated by conventional acceptance tests.

This rock is a fine-grained calcareous dolomite or dolomitic limestone with an acid insoluble content of 5 to 15 percent and containing approximately equal proportions of calcite and dolomite. Bulk specific gravity was 2.70 and absorption 0.7 percent. Pore volume, as measured by the mercury vacuum pressure method, was found to be very small.

In the acid insoluble portion, clay minerals present are illite and lesser amounts of chlorite together with a small proportion of finely divided quartz, feldspar, and graphitic material. In the more highly calcitic carbonate rock used as a nonreactive reference, the acid insoluble material, though somewhat smaller in amount, was found to have a very similar composition.

The bed at a depth of 24 to 30 ft produced a relatively small expansion of the concrete. Its dolomite content is much higher than the calcite content. It is a slightly green rock with an acid insoluble content of about 40 percent. The acid insoluble constituents are similar to those in the upper horizons except that this bed contains, in addition, a considerable quantity of silt-size and very fine sand-size particles of quartz. Less than 5 percent of this rock was considered physically unsound. Pore size was also very small but absorption was relatively high, about 3 percent.

The 30- to 36-ft layer in the same quarry produced even less expansion of concrete than the "green" rock. It is still more dolomitic and has a higher absorption, 6 percent. The acid insoluble portion is about 30 percent.

The rocks from the other horizons in the two quarries varied in composition from dolomitic limestones to calcitic dolomites with no clear-cut relation between reactivity and composition. The relatively rare occurrence in nature of carbonate rocks having roughly equal proportions of calcite and dolomite (11) suggests a constitutional instability which may be responsible for reactivity with

Variations in amounts of each of the "reactants" (high alkali cement and reactive rock) produced the corresponding proportional changes in rate and degree of expansion of the concretes.

Variation in the Carbonate Rock.—Stratigraphically the rocks in the two quarries are of Ordovician age and belong to the Black River formation. The rock from the several operating or natural horizons in each of the two quarries showed, on the basis of expansion of concrete prisms, variable degrees of reactivity. These differences are compared in Table 2 with values for corresponding samples made with a low alkali cement. The test samples were continuously exposed to 100 percent relative humidity and 73 F.

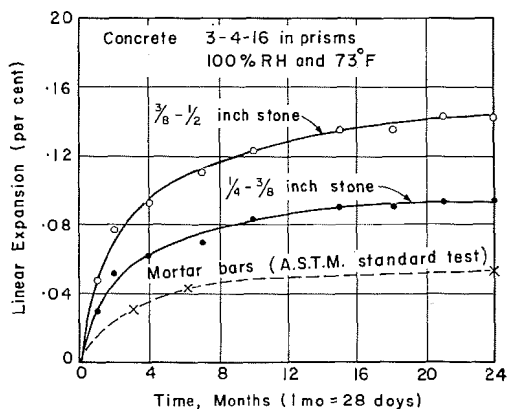


Figure 6. Effect of maximum size of reactive limestone on expansion of concrete and mortar bars.

alkalies. In certain of the rocks soaked in alkaline solution a reduction in dolomite content was observed on X-ray films. In the case of a composite sample of the 0- to 24-ft series the strong dolomite lines have almost completely disappeared while three new lines, attributed to brucite, have appeared on the pattern. In the 10½- to 12-ft bed the dolomite lines are weakened after the alkaline attack on the rock (Fig. 7). The highly dolomitic rock at Kingston produced only a small abnormal expansion, and the highly calcitic reference rocks showed no reactivity. The X-ray patterns show no apparent change before or after alkaline attack.

The rocks that produced only small expansion of concrete (24 to 30 ft layer) were combined with various proportions of the nonreactive reference rock, both as coarse aggregate and as fine aggregate. In no case was a pessimum obtained. Combinations of the very reactive rock and the least reactive rock produced dilution effects only.

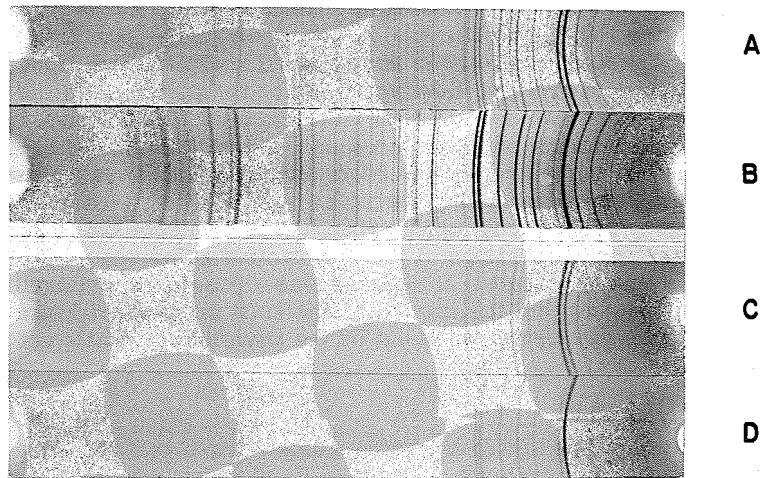
Extensive studies are being continued by the Division in an attempt to determine the mechanism of the reaction.

Influence of Environment

Moisture.—Laboratory and field observations showed that the Kingston reaction was dependent on a moist environment as are alkali-silica reactions. In the concrete prism test maximum rate and degree of expansion was obtained by continuous exposure to near 100 percent relative humidity. Continuous immersion in water at the same temperature (73 F) gave similar expansion values for concrete prisms. This dependency on moisture is shown by the expansion values plotted in Figure 8. Duplicate 3- by 4- by 16-in. concrete prisms were made with the reactive rock and with a nonreactive limestone rock as a reference, each with a high alkali (1.19 percent) and a low alkali

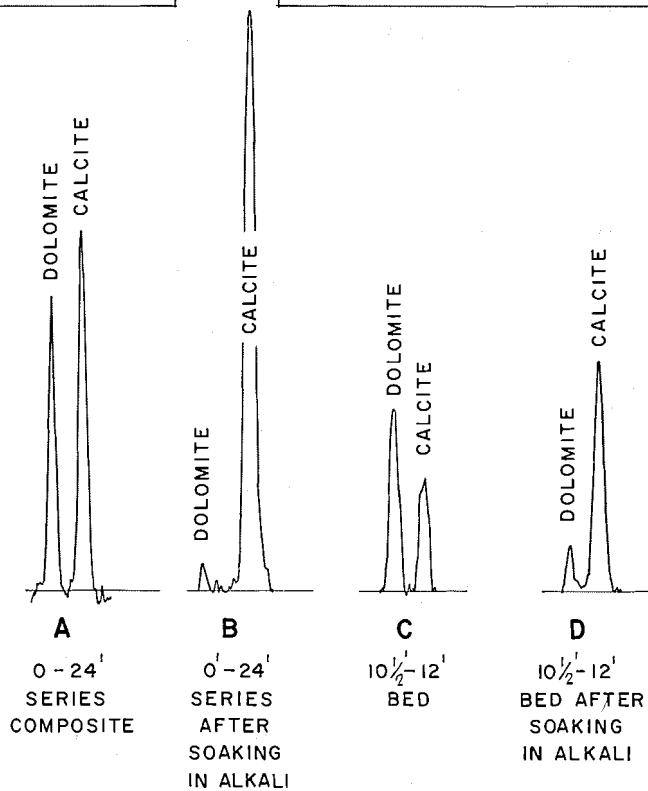
TABLE 2
EXPANSION OF CONCRETE MADE WITH ROCK FROM DIFFERENT
LEVELS IN THE TWO QUARRIES

Prisms, 3 by 4 by 16 in.		Mix = 1:2:3 ¹ / ₄			
Condition: 100 percent relative humidity and 73 F		Max. size rock = ³ / ₄ in.			
		Slump = 1 in.			
	Percent Cement	Linear Expansion (percent)			
Quarry Level (ft)	Alkali as Na ₂ O	6 months	12 months	18 months	24 months
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
13-15	1.19	0.050	0.051	-	0.060
	0.31	0.014	0.019	0.023	0.026



Λ BRUCITE LINES

PHILIPS POWDER CAMERA 114.6 MM DIA.



DOUBLE-BEAM RECORDING MICRODENSITOMETER TRACE OF STRONGEST
DOLOMITE AND CALCITE LINE. JOYCE, LOEBL & CO. LTD.
MODEL E12 MK III WALKER DESIGN EXPANSION OR RECORDING
RATIO 1:5 OBJECTIVE 0.28 N.A. 16 MM.

Figure 7. Dedolomitization on treatment with alkali.

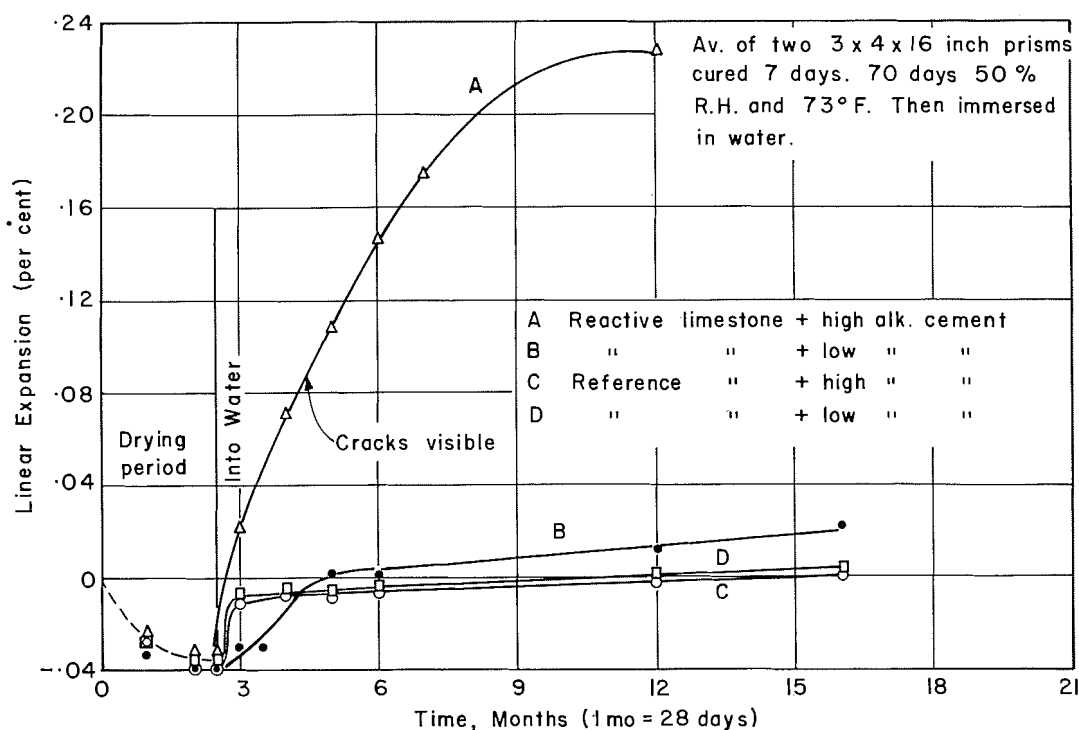


Figure 8. Expansion of test concretes following initial drying period.

cement (0.36 percent). After curing 7 days the prisms were conditioned at 50 percent relative humidity and 73 F for 63 days, after which they were immersed in water. All the specimens contracted normally and by the same amounts during the drying period. Once immersed in water, however, the concrete made with the reactive Kingston rock and the high alkali cement began to expand rapidly while the one with the low alkali cement showed the usual slight expansion. The initial drying period appeared to have had no permanent effect on the subsequent reaction under moist conditions.

Temperature.—The influence of temperature on the reaction is shown in Figure 9. Duplicate concrete prisms made with the reactive carbonate rock and with high and low alkali cements were conditioned at near 100 percent relative humidity at temperatures of 73, 100, and 130 F. With the high alkali cement (1.19 percent) the increase in the rate and degree of expansion with increase in temperature from 73 to 100 F, and the apparent reversion at 130 F indicate that the temperature effect in the reaction is remarkably similar to that of the alkali-silica type of reaction (12). With the low alkali cement (0.31 percent) the expansion became excessive at the higher temperature, suggesting that, in the field, for a combination of a high temperature and a moist environment, the cement alkali must be very low to prevent excessive expansion and cracking.

Cycling Involving Moisture and Temperature.—The rate and degree of expansion of concrete containing Kingston limestone as coarse aggregate have been compared for different exposure conditions (1). A modified Scholer test (wetting for 6 hours at room temperature and drying for 6 hours at 130 F) produced a somewhat higher expansion than exposure to 100 percent relative humidity at 73 F. The expansions of corresponding specimens subjected to slow freeze-thaw cycling (freezing in air) and to outside exposure were much lower. In the wetting-drying test, the expected retardation of the reaction due to drying was apparently more than offset by the high drying temperature. In the freeze-thaw test the observed retardation was apparently caused by the lower temperature.

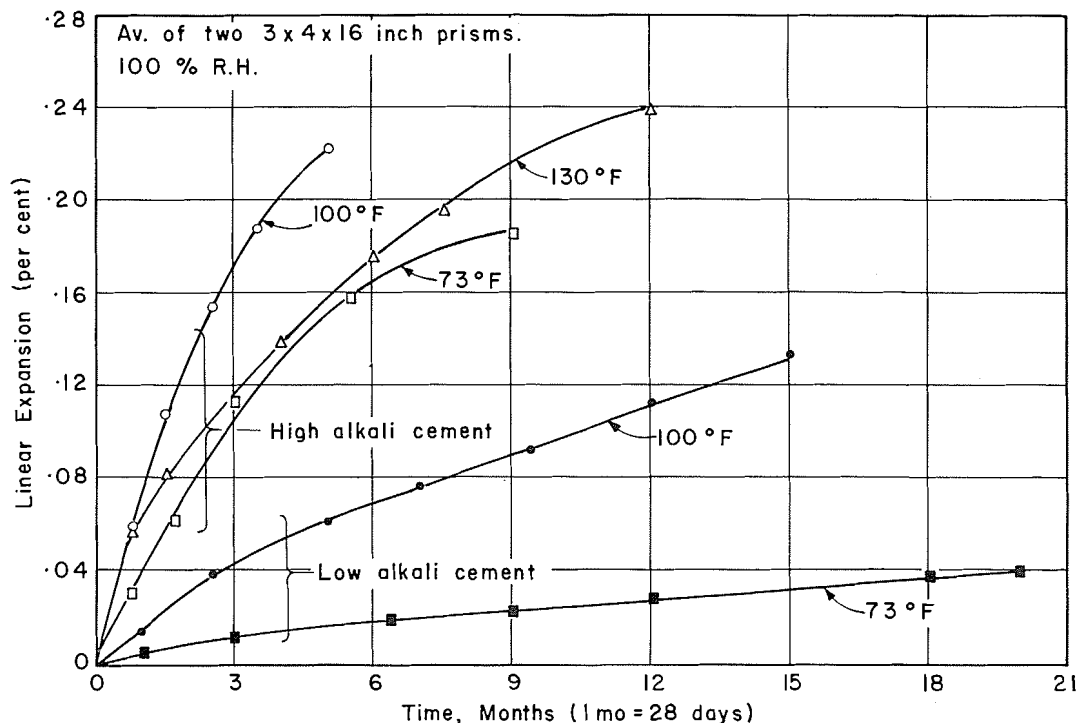


Figure 9. Effect of temperature on expansion of concrete made with reactive carbonate rock.

The normal Scholer test (16 hours wetting at room temperature and 8 hours drying at 130 F) was carried out on non-air-entrained concretes made with low and high alkali cements and coarse aggregate from each of the operating horizons in the two quarries. The expansions at various ages are shown in Table 3. These values are comparable with those exposed to 100 percent relative humidity and 73 F in Table 2. These two methods of test appear, therefore, to reveal reactivity of the rock through expansion of concrete.

Companion specimens subjected to freeze-thaw cycling (6 hours freezing at 18 F and 6 hours thawing at room temperature) showed the usual lower rate of expansion for the concretes made with the reactive rocks and the high alkali cements. With low alkali cements, only the 30- to 36-ft bed in Quarry A showed low durability. Air-entrained concrete made with the very reactive rock and a low alkali cement showed no sign of disintegration after more than 1,000 cycles.

EXPANSION OF CARBONATE ROCK IN ALKALINE SOLUTION

The presence of a considerable clay fraction in the reactive Kingston limestone suggested the possibility that relatively weak clay seams were opened up to the strong alkali solution present in concrete made with high alkali cement, and that the expansion of the concrete may therefore have resulted from cracking of the rock itself rather than from an inherent tendency to expand.

Samples of the Kingston rock and of reference carbonate rock were immersed in 2-molar alkaline solution, made up of nearly equal parts of sodium and potassium hydroxide and containing 0.01 equivalents of calcium ion and 0.15 equivalents of sulfate ion.

In one experiment 500 gm of the reactive crushed rock ($\frac{1}{2}$ to $\frac{3}{4}$ in.) was vacuum saturated with the above solution and compared with a control specimen of inactive carbonate rock treated in the same way. The volume changes of the solutions were measured and, by subtracting the volume change of the control specimen from the test

TABLE 3
RESULTS OF SCHOLER TEST ON ROCKS FROM SELECTED
LEVELS IN THE QUARRIES

Mix: 1:2:3 $\frac{1}{4}$		Cure before cycling:			
Slump = 2 to 3 in.		7 days moist room			
Max size = $\frac{3}{4}$ in.		21 days drying, 50 percent relative humidity and 73 F.			
Quarry Level (ft)	Percent Cement Alkali as Na ₂ O	Linear Expansion (percent)			
		3 months	6 months	12 months	18 months
Quarry A					
0-24	1.19	0.132	0.182	0.234	-
	0.36	0.018	0.029	0.032	0.033
24-30	1.19	0.007	0.014	0.022	0.024
	0.36	0.004	0.012	-	0.013
30-36	1.19	0.001	0.011	0.022	0.024
	0.36	0.003	0.009	0.012	0.012
36-48	1.19	0.106	0.158	0.200	0.220
	0.36	0.012	0.026		0.033
Quarry B					
0-12	1.19	0.043	0.051	0.070	0.074
	0.36	0.016	0.020	0.026	0.028

specimen at each reading, small fluctuations due to temperature change and residual absorption were considered as cancelling out. The net increase in volume exhibited by the reactive rock was remarkably similar to the expansion curves for the affected concretes previously described. Net expansions were: 0.06 at 1 month, 0.10 at 2 months, 0.15 at 4 months, and 0.22 at 8 months. An estimated one-sixth of the rock had cracked up but this should not have affected the total volume of solid plus solution.

Rock prisms, measuring 1 $\frac{1}{2}$ by 5 $\frac{3}{4}$ in., were cut from several selected beds in Quarry A and from reference carbonate rocks. The ends were planed and polished to permit the fitting of special plates for measuring length changes in a comparator. Prisms were immersed continuously in 2-, 0.44-, and 0.06-molar alkaline solutions and in water. The small volume change due to wetting was corrected for by taking as zero expansion the readings after one-day immersion.

Although many of the reactive prisms cracked, mainly along bedding planes, after only a week or two in the 2-molar solution, some prisms remained uncracked and volume changes were measured up to one year of age. Typical plots are shown in Figure 10 for the 6- to 7-ft bed in Quarry A.

The expansion of the rock in the 2-molar alkaline solution was remarkably similar in rate and degree to the expansion of concretes made with the reactive rock and a high alkali cement. The 0.44-molar solution had no effect but did show a slight tendency to produce expansion after 9 months. This solution did produce a considerable expansion of a more reactive rock, the 10 $\frac{1}{2}$ - to 12-ft bed. The reference rock, not shown, yielded values closely corresponding to the lowest curves of Figure 10.

These results would suggest that the alkali, although producing cracking at planes of weakness, also produces an expansion of the reactive rock itself. This method would appear to be a means of determining the type of reactivity exhibited by the Kingston dolomitic limestone.

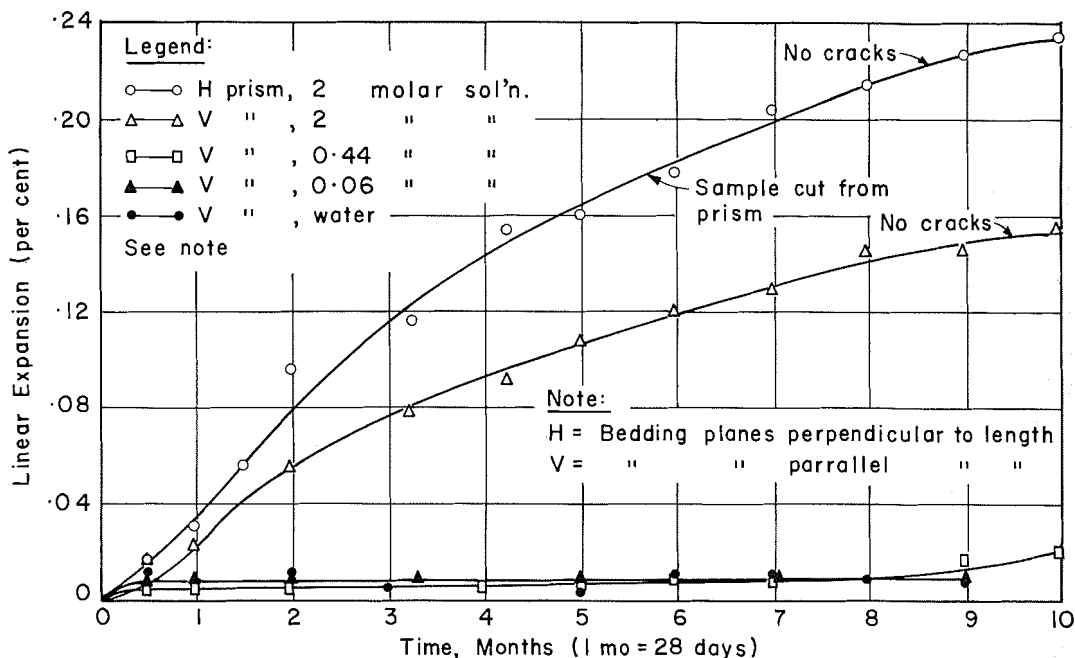


Figure 10. Expansion of limestone prisms in alkaline solutions, 6 - 7' bed, Quarry A.

SUMMARY AND CONCLUSIONS

The alkali-reactivity of the Kingston carbonate rock was found to be similar in certain important respects to the alkali-silica type of reaction. Certain characteristics were, however, markedly different.

The points of similarity were: (1) the specific influence of alkali content, whether it derives from the cement or is added, (2) the more aggressive influence of the sodium than the potassium hydroxide, (3) the influence of temperature, with evidence of an optimum, (4) the direct influence of moisture, and (5) the abnormal expansion of concrete, followed by map-cracking where moisture conditions vary at two surfaces.

Characteristics that show some limited degree of similarity were: (1) rate and degree of expansion were apparently higher in this case; (2) decrease in expansion with decrease in particle size of aggregate, apparently due to break-up at planes of weakness as well as to increase in surface area for a fixed amount of alkali; (3) rim formation present but different in appearance from the alkali-silica type; (4) microscopic evidence of fracturing of paste and aggregate but difference in appearance of affected areas.

Distinguishing features were: (1) absence of significant quantities of gel; pore volume was extremely small, and amount of silica very small, hence it is not likely that failure to detect gel is due to its distribution throughout the pores; (2) absence of minerals or rock types known to react deleteriously with cement alkali; (3) failure of alkali-silica reaction inhibitors to control this alkali-carbonate rock reaction; (4) increase in water-cement ratio apparently does not increase rate of reaction; (5) uncracked parts of the affected concrete appear to remain intact, even after many years.

The Kingston carbonate reaction is not detectable by the standard ASTM tests. It may be detected by exposing concrete prisms made with the suspected rock and a high alkali cement to near 100 percent relative humidity and 73 F conditions, or to the Scholer test. It may also be detected by measuring expansions of the rock in alkaline solution.

As a tentative conclusion rocks composed of near equal proportions by weight of dolomite and calcite may be regarded as suspect and it seems possible that a connection exists between the expansive reactivity and the dedolomitization reaction (replacement of dolomite by calcite and brucite).

Work is continuing to establish whether the reactivity with alkali is controlled by the composition, texture, or structure of the rock.

REFERENCES

1. Swenson, E.G., "A Canadian Reactive Aggregate Undetected by ASTM Tests." Amer. Soc. for Testing Materials, Bulletin No. 226 (Dec. 1957).
2. Lemish, J., Rush, F.E., and Hiltrop, G.L., "Relationship of Physical Properties of Some Iowa Carbonate Aggregate to the Durability of Concrete." HRB Bull. 196, pp. 1-16 (1958).
3. 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).
4. Mielenz, R.C., Greene, K.T., and Benton, E.J., "Chemical Test for Reactivity of Aggregate with Cement Alkalis; Chemical Processes in Cement-Aggregate Reaction." Proc., Amer. Concrete Inst., Vol. 44, pp. 193-221 (1948).
5. Chaiken, B., and Halstead, W.J., "Correlation between Chemical and Mortar Bar Tests for Potential Alkali Reactivity of Concrete Aggregates." HRB Bull. 239, pp. 24-40 (1960).
6. Mielenz, R.C. Private communication.
7. Mather, Bryant. Private communication.
8. Scholer, C.H., "A Wetting and Drying Test for Predicting Cement-Aggregate Reaction." Kansas State College Bulletin, Circular No. 2 (Aug. 15, 1950).
9. Davis, C.E.S., "Studies in Cement-Aggregate Reaction, XXVI Comparison of Effect of Soda and Potash on Expansion." Australia, Jour. of Applied Science, Vol. 9, No. 1, pp. 52-62 (1958).
10. McCoy, W.J., and Caldwell, A.G., "New Approach to Inhibiting Alkali-Aggregate Reaction." Proc., Amer. Concrete Inst., Vol. 47, p. 693 (1951).
11. Pettijohn, F.J., "Sedimentary Rocks." Harper Bros., New York, second ed. (1957).
12. Lerch, W., "Chemical Reactions. Concrete Aggregates." Amer. Soc. for Testing Materials, Special Technical Bulletin No. 169, pp. 334-45 (1956).