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## ALKALI-CARBONATE ROCK REACTION

BY

E. G. SWENSON AND J. E. GILLOTT

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## LA REACTION ALCALI-CARBONATE DES ROCHES

### SOMMAIRE

Cette étude constitue une revue de huit années de recherches sur la réaction alcali-carbonate des roches. Ces recherches ont été faites par la Division des recherches en bâtiment du Conseil national de recherches, Ottawa, Canada et la plus grande partie de cette étude a été ou sera publiée dans d'autres revues. On expose succinctement le cas de Kingston qui le premier a permis de déceler une dilatation excessive du béton causée par la réactivité de l'alcali-carbonate sur de gros agrégats de calcaire dolomitique. On décrit des études plus poussées dans ce domaine, de même que des recherches sur la nature de la réaction, des méthodes d'essai et d'identification et quelques hypothèses relatives au mécanisme de la réaction et de la dilatation.

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## Alkali-Carbonate Rock Reaction

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

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-

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.

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.

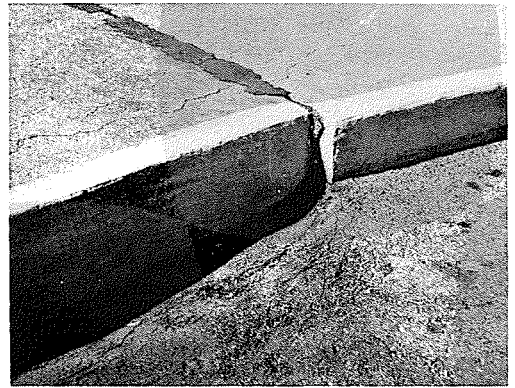


Figure 1. Expanding concrete resulted in closing of joints, buckling, and map-cracking.

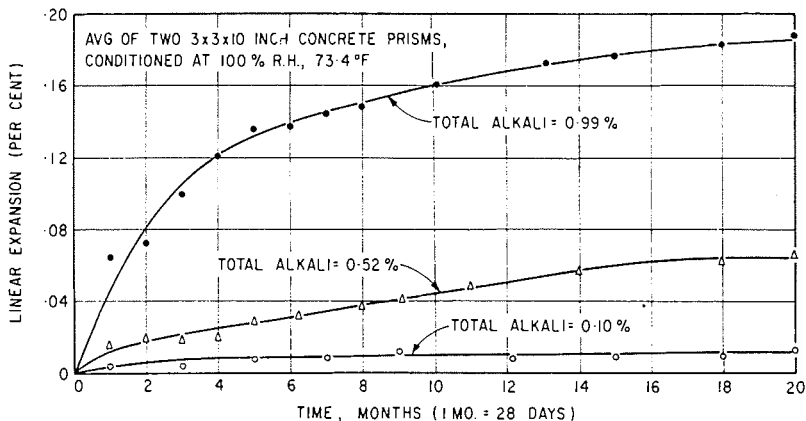


Figure 2. Reactive coarse aggregate in concrete produced expansion according to content of cement alkali.

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<sup>1</sup> MADE WITH ROCK FROM  
DIFFERENT LEVELS IN QUARRIES A AND B

Quarry Level (ft)	Cement Alkali, as Na <sub>2</sub> O (%)	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
	0.36	0.002	—	0.006	—
30-36	1.19	0.005	0.009	0.010	0.012
	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

<sup>1</sup> Prisms, 3 x 4 x 16 in.  
Condition: 100% R.H.  
and 73 F

Mix = 1:2:3<sup>1</sup>/<sub>4</sub>  
Max. size rock = 3/4 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  $\text{Na}_2\text{O}$ ). 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  $\text{Na}_2\text{O}$ ) 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 normalfield 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



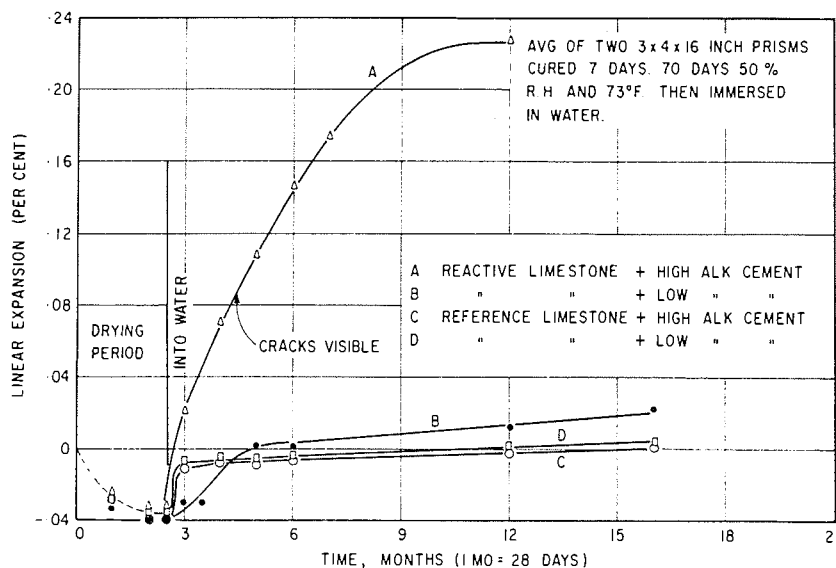


Figure 4. Expansion of test concretes following initial drying period.

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  $\text{Na}_2\text{O}$ ) 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.

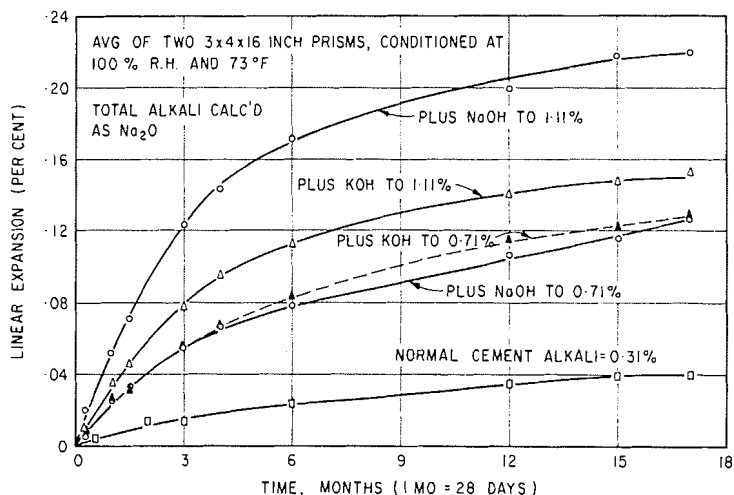


Figure 5. Concrete expansion with reactive carbonate rock and low alkali cement with added alkalis.

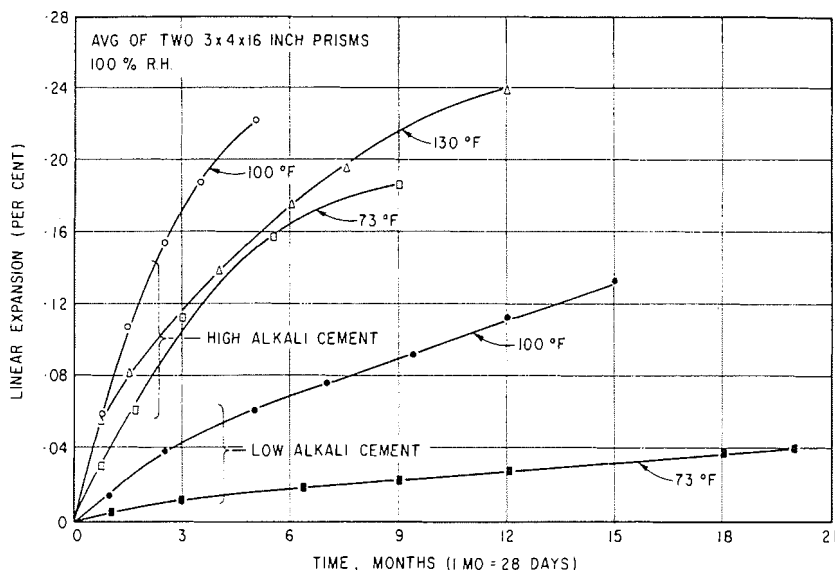


Figure 6. Effect of temperature on expansion of concrete made with reactive carbonate rock.

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  $1\frac{1}{2}$  by  $1\frac{1}{2}$  by  $5\frac{3}{4}$  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.

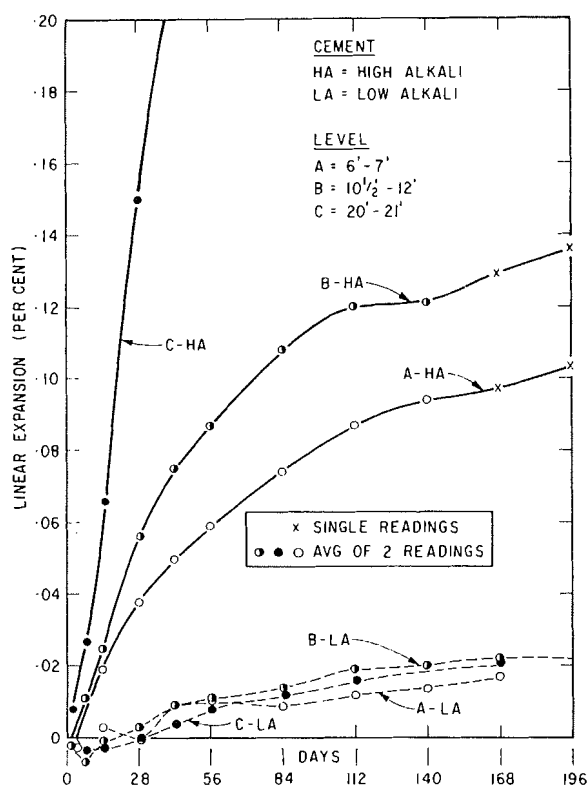


Figure 7. Different expansions in concrete caused by Kingston aggregate from specific strata in quarry A.

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  $\text{CaCO}_3$  (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.

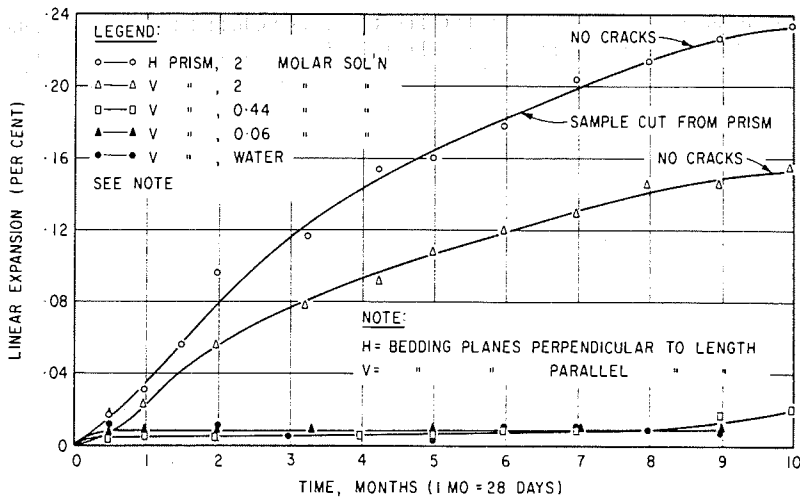


Figure 8. Expansion of reactive carbonate rock prisms in alkaline solutions of different concentrations (6- to 7-ft bed, quarry A).

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-

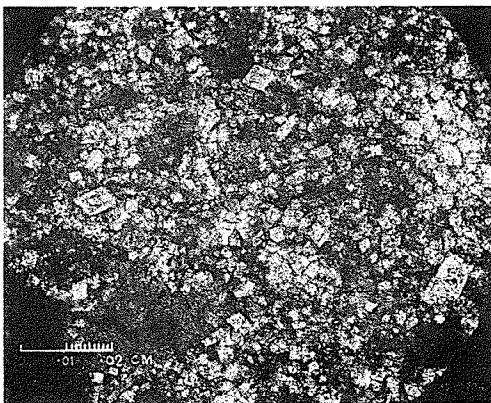


Figure 9. Photomicrograph of alkali-reactive dolomitic limestone, Kingston, Ont.



Figure 10. Photomicrograph of reactive rock from Kingston, Ont., showing dolomite crystals 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.

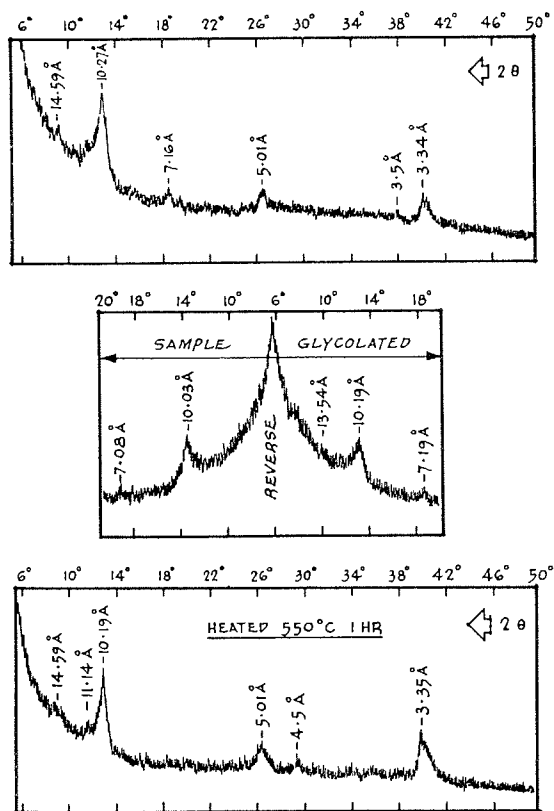
### Mineralogy

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  $\text{CaCl}_2$  to replace hydrogen with calcium ions on the exchange sites.



SETTING OF GENERAL ELECTRIC CO. DIFFRACTOMETER  
XRD - 5

EXIT SLIT: 3°	TIME CONSTANT: 2
SOLLER SLITS: MEDIUM RESOLUTION	X-RADIATION: CR
RECEIVING SLIT: 0.2°	FILTER: V
RESPONSE: LINEAR	KV: 50
FULL SCALE DEFLECTION: 200 C.P.S.	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 absorption.

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 photo-elastic 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  $\text{Na}_2\text{CO}_3$  formed in the reaction should pass into solution. There are hydrated double salts of large cell volume such as gaylussite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ ) and pirssonite ( $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$ ). 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  $\text{Na}_2\text{CO}_3$  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.

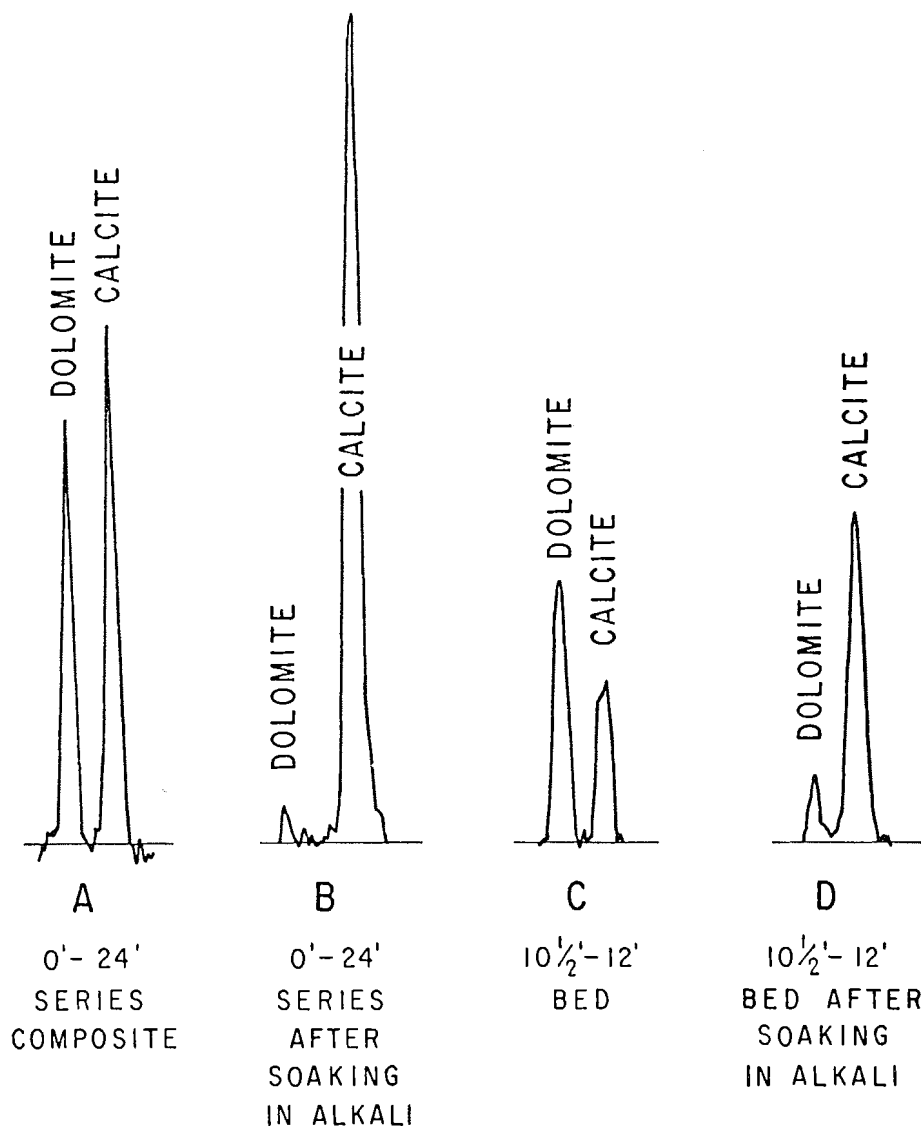


Figure 12. Dedolomitization on treatment with alkali.

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  $\text{Na}_2\text{CO}_3$  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:

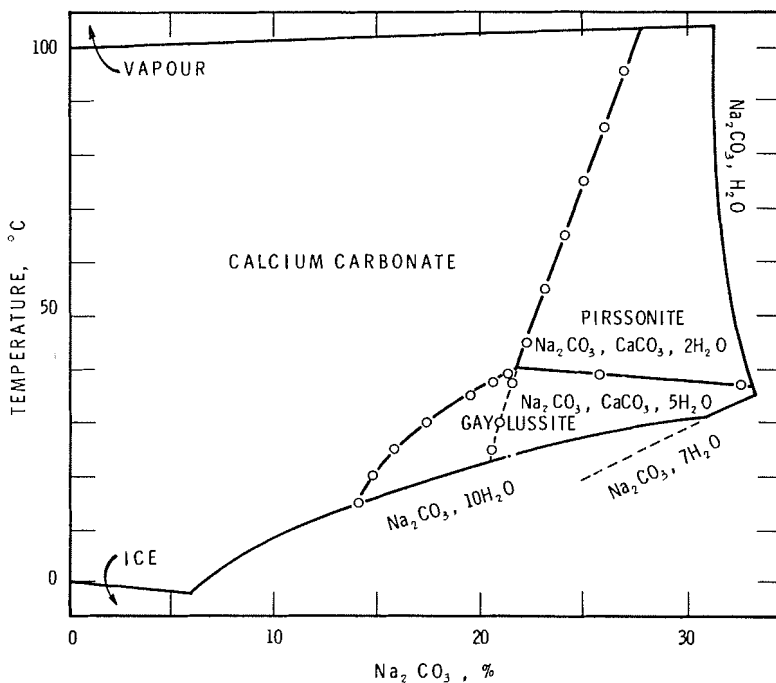


Figure 13. The system sodium carbonate-calcium carbonate-water (after Bury and Redd (23)).

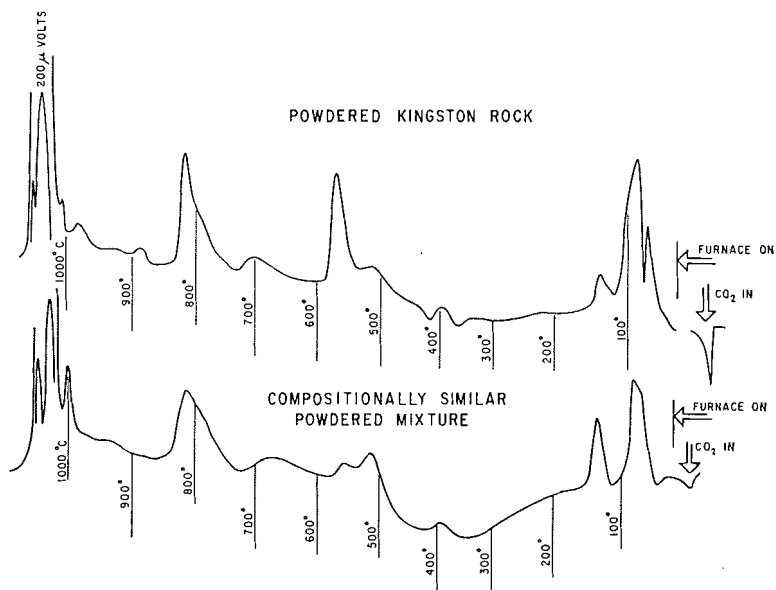


Figure 14. Thermograms of expansive Kingston rock and compositionally similar, non-expansive mixture after treatment in 2M NaOH for 14 days. Samples dried in air for 1 hour.

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 crystallinities 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  $\text{CaCl}_2$ . 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 paper (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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