

## *Part I. THEORETICAL STUDIES*

# Alkali Reactivity of Dolomitic Carbonate Rocks

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of the alkali-reactive carbonate rocks in field and laboratory concretes is described, and previously published and unpublished research concerning the causes and mechanisms of reactivity is reviewed and discussed.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

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The compilation of the current knowledge concerning the rocks of this type has necessitated the inclusion of previously unpublished work.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

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

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 In addition, previously published and unpublished studies concerning the causes and mechanisms of reactivity are reviewed and discussed, and tests for the recognition of the reactive rocks are summarized.

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

## EXPANDING ROCKS

Nature of Problem

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

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

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

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

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

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

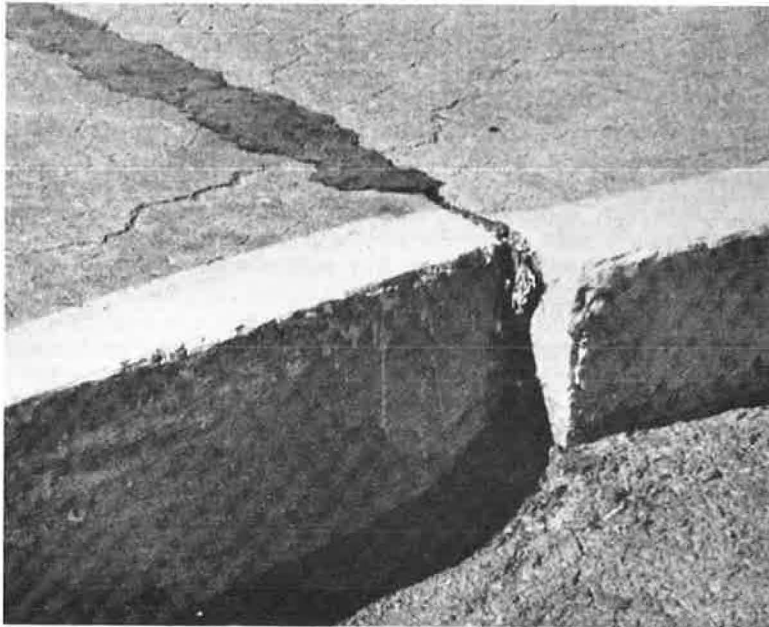


Figure 1. Map cracking and expansion of concrete in Kingston, Ontario, reflects the expansion of the alkali-reactive aggregate particles (2).

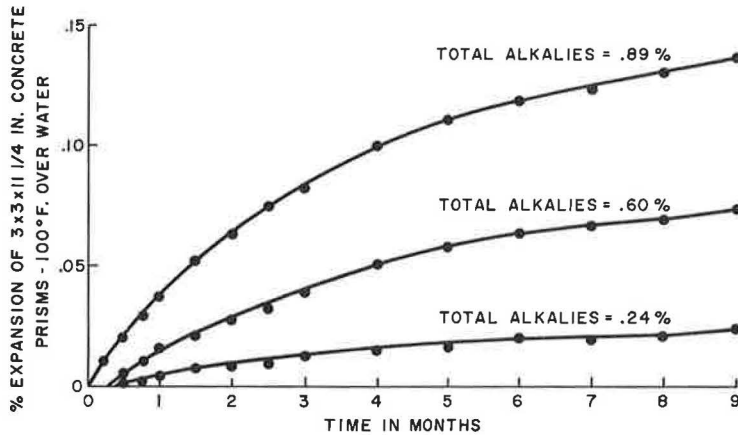


Figure 2. Rate of expansion of concrete is influenced by alkali content ( $\text{Na}_2\text{O}$  equivalent) of cement (7).

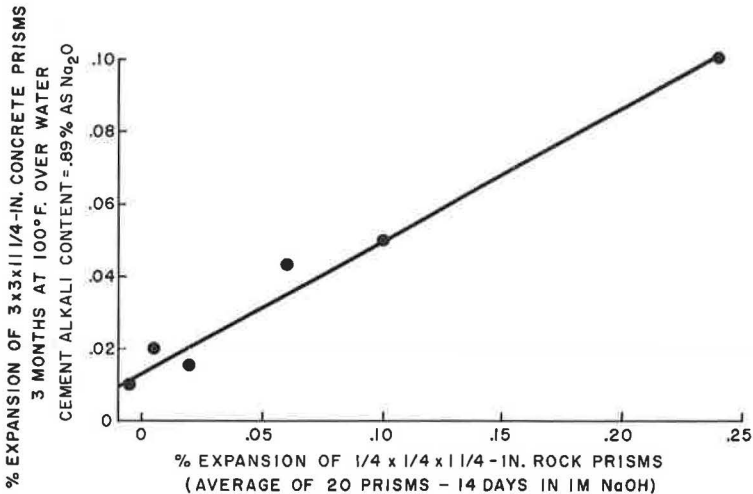


Figure 3. Expansion of small rock prisms in alkaline solution correlates well with expansion of concretes made using these rocks as aggregate (7).

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

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

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

#### Nature of Expansive Rocks

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

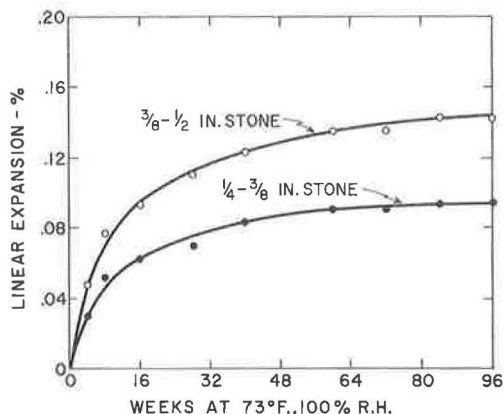


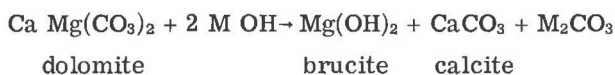
Figure 4. Effect of maximum size of reactive limestone on expansion of concrete (3).

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

#### Mechanisms of Reactivity

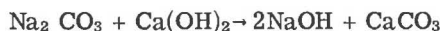
Dedolomitization Reaction.—X-ray diffraction studies of expansive rocks which have been reacted with solutions of the alkali metal hydroxides show a decrease in the amount of dolomite present, an increase in calcite content, and the appearance of brucite. Further laboratory studies by Hadley (4) have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

This reaction can be written as



in which M represents K, Na, or Li.

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



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

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

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

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

#### Physical Characteristics of Expansive Rocks.—A number of the expansive rocks

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

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

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

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

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

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

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



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

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

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

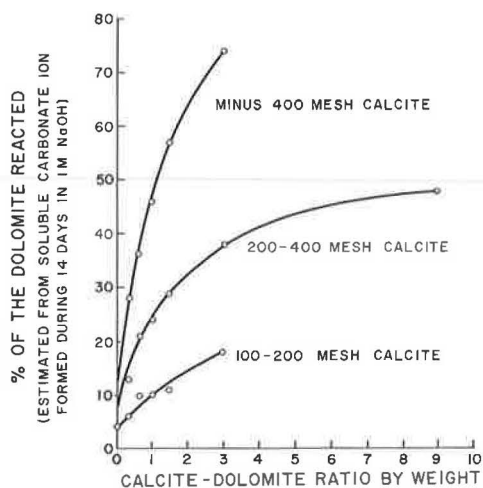


Figure 5. Rate of reaction of 200-400 mesh dolomite in laboratory mixtures is a function of amount and grain size of admixed calcite.

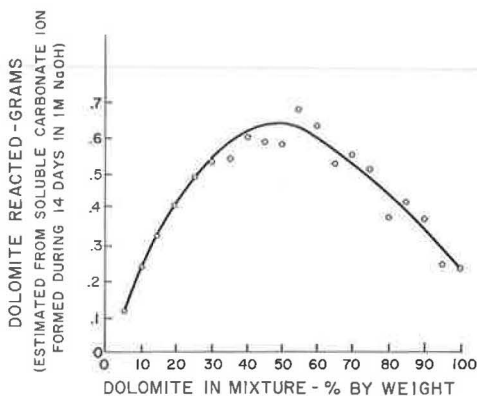


Figure 6. The greatest amount of dolomite was reacted in mixtures containing approximately equal amounts of calcite and dolomite.

TABLE 1

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

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

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

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

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

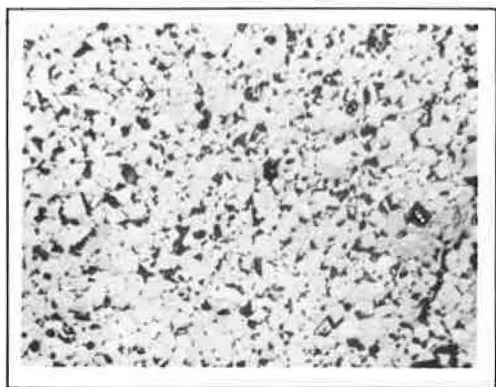
Role of Clay in Expansion of Reactive Rocks.—One of the outstanding characteristics of the reactive rocks is their high clay content. (Clay is used here as including all non-carbonate material in the rock having an equivalent spherical diameter of two microns or less. Clay contents were normally determined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

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

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

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

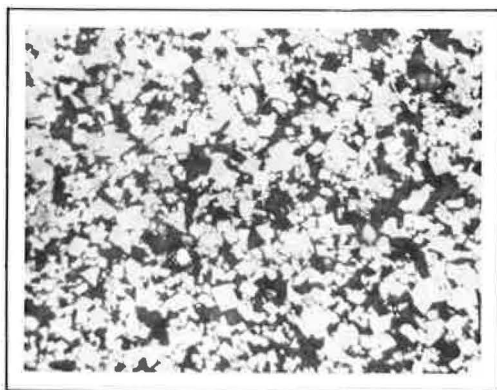
As the percentage of clay in the rock increases, there is a progressive disruption of the internal carbonate skeleton. As shown by the relative expansions of the rocks



APPROXIMATELY 7% CLAY  
EXPANSION IN ALKALI = .07%

100  $\mu$

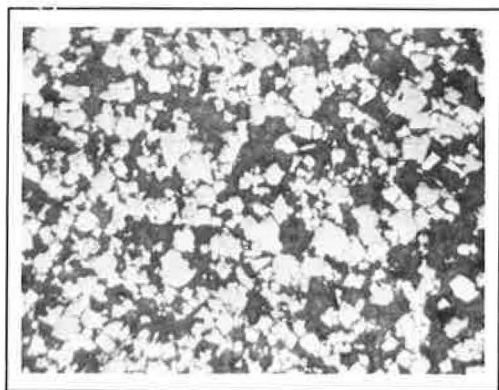
Figure 7. In rocks with low clay contents interpenetrating dolomite crystals form rigid structural framework and expansion is low.



APPROXIMATELY 15% CLAY  
EXPANSION IN ALKALI = .74%

100  $\mu$

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



APPROXIMATELY 25% CLAY  
EXPANSION IN ALKALI = 1.20%

100  $\mu$

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

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

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

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

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

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

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

lessens the ability of the rock to withstand the expansive forces generated by the de-dolomitization reaction.

### Tests for Recognition of Expansive Carbonate Rocks

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

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

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

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

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

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

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

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

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

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

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

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



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

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

## RIM-DEVELOPING ROCKS

### Nature of Problem

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

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

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

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

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

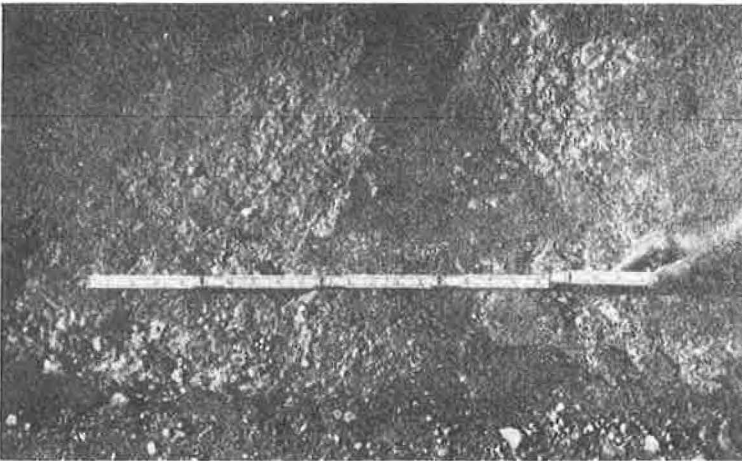


Figure 10. Deterioration of this Iowa pavement attributed to rim-developing carbonate coarse aggregate (14).

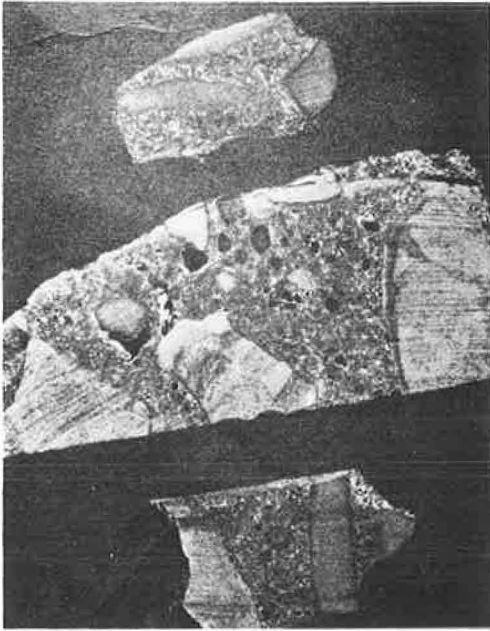


Figure 11. Typical reaction rims in concrete (14).

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

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

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

TABLE 2

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

Specimens: 3- by 6-in. concrete cylinders.

Aggregate: Elgin, Illinois gravel and rim-developing Jeffersonville limestone from Indiana.

$\frac{3}{4}$ -in. maximum size of aggregate.

Nominal cement content: 6.5 bags per cu yd.

Water-cement ratio:  $4\frac{1}{2}$  gal per bag. Slump 1-2 in.

Curing: 1 day in molds at 73 F, 100% R.H. then to designated storage.

Each value represents the average of three specimens, one from each of three rounds.

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

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

### Mechanisms of Reactivity

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

TABLE 3  
RESULTS OF LATHE EXPERIMENT

Mean Distance from Center of Bar (in.)	Composition by Weight (%)							
	On Ignited Basis							Dried at 110 C
	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	CO <sub>2</sub>
(a) Original Rock								
—	4.19	1.34	58.97	34.44	0.16	0.21	nil	81.47
(b) Original Paste								
—	20.34	8.23	67.66	0.88	0.21	0.41	1.79	0.32
(c) Paste								
1.662	21.00	8.60	67.21	1.36	0.14	0.28	0.97	9.98
1.500	20.39	8.15	67.84	1.18	0.09	0.10	1.91	1.57
1.250	20.41	8.17	67.88	1.13	0.10	0.10	1.86	0.70
1.000	20.42	8.22	67.80	1.26	0.10	0.11	1.84	0.88
0.750	20.39	8.15	67.78	1.11	0.10	0.12	2.00	0.31
0.700	20.42	8.05	67.88	1.04	0.11	0.13	2.06	0.83
0.650	20.38	8.13	68.34	1.18	0.18	0.25	1.34	3.09
0.640	20.59	8.26	68.10	0.76	0.22	0.27	1.95	2.95
0.630	20.67	8.37	66.95	0.10	0.39	0.58	1.81	12.07
(d) Rock								
0.623	5.00	1.53	57.38	32.79	1.71	1.58	nil	76.78
0.611	4.77	1.35	58.72	33.29	0.67	0.95	nil	79.95
0.597	4.52	1.41	58.82	33.63	0.49	0.70	nil	81.24
0.581	4.33	1.38	59.02	33.66	0.38	0.55	nil	80.34
0.567	4.14	1.29	59.58	34.16	0.48	0.34	nil	81.37
0.550	4.04	1.24	59.70	33.54	0.40	0.28	nil	79.54
0.500	3.83	1.19	60.31	33.06	0.23	0.15	nil	79.32
0.400	3.31	1.32	59.93	33.65	0.09	0.09	nil	81.32
0.300	3.22	1.17	60.31	34.16	0.08	0.09	nil	83.62
0.194	3.50	1.25	59.88	34.39	0.09	0.09	nil	83.26

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

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

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

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

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

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

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

Although a mechanism of silica polymerization on clay minerals is not unreasonable and may well occur in natural geologic environments, it is felt that the high pH of the concrete environment largely precludes the large-scale polymerization postulated. An experiment was performed in which illite, montmorillonite and kaolinite clays were individually agitated with sodium-silicate solution (0.75M Na<sub>2</sub>O, 0.33M SiO<sub>2</sub>) for three weeks. Analysis of the solutions showed that rather than removing silica from solution, all of the clays tested were actually somewhat soluble and the silica contents of the solutions were increased (Table 4).

TABLE 4  
COMPARATIVE SOLUBILITY OF CLAY MINERALS IN SODIUM  
SILICATE SOLUTION AND EFFECTIVENESS OF BRUCITE  
IN REMOVING SILICA FROM SOLUTION<sup>a</sup>

Absorbate	SiO <sub>2</sub> in Sol. (gm/gm of sol.)
Initial sodium silicate solution <sup>b</sup>	0.0210
Montmorillonite	0.0233
Illite	0.0219
Kaolinite	0.0213
Brucite	0.0157

<sup>a</sup>4 grams absorbate in 40 ml of solution for 21 days.

<sup>b</sup>0.75M NaOH, 0.33M SiO<sub>2</sub>.

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

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

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

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

#### Rocks Which Develop "Negative" Reaction Rims

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

#### Tests for Recognition of Rim-Developing Rocks

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

2. Imbedded cubes. A relatively rapid test for rim development can be made by imbedding  $\frac{1}{2}$ -in. cubes of rock in  $1- \times 1- \times 1\frac{1}{4}$ -in. mortar bars made with silica sand and a cement of high alkali content. The mortar bars are stored for 8 weeks in cans over water at 100 F. At the end of the storage period the bars are cut in half longitudinally with a diamond saw and etched with dilute hydrochloric acid. The presence of acid-resistant reaction rims is determined by visual examination of the etched bar. A typical test specimen is shown in Figure 12. Similar tests have been used by Bisque and Lemish (10).

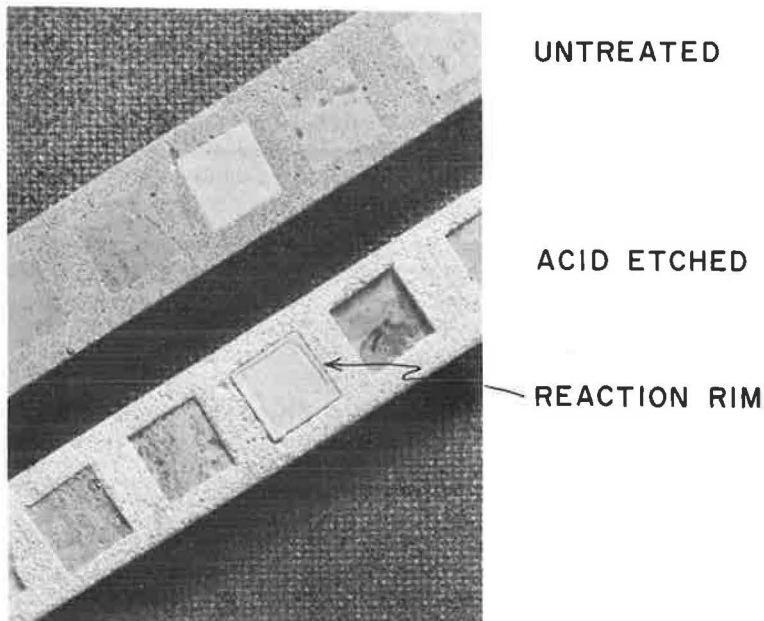


Figure 12. Rock cubes embedded in mortar bars. Development of reaction rims revealed by acid etching of bars.

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

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

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

#### RELATIONSHIP BETWEEN RIM-DEVELOPING AND EXPANSIVE ROCKS

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

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

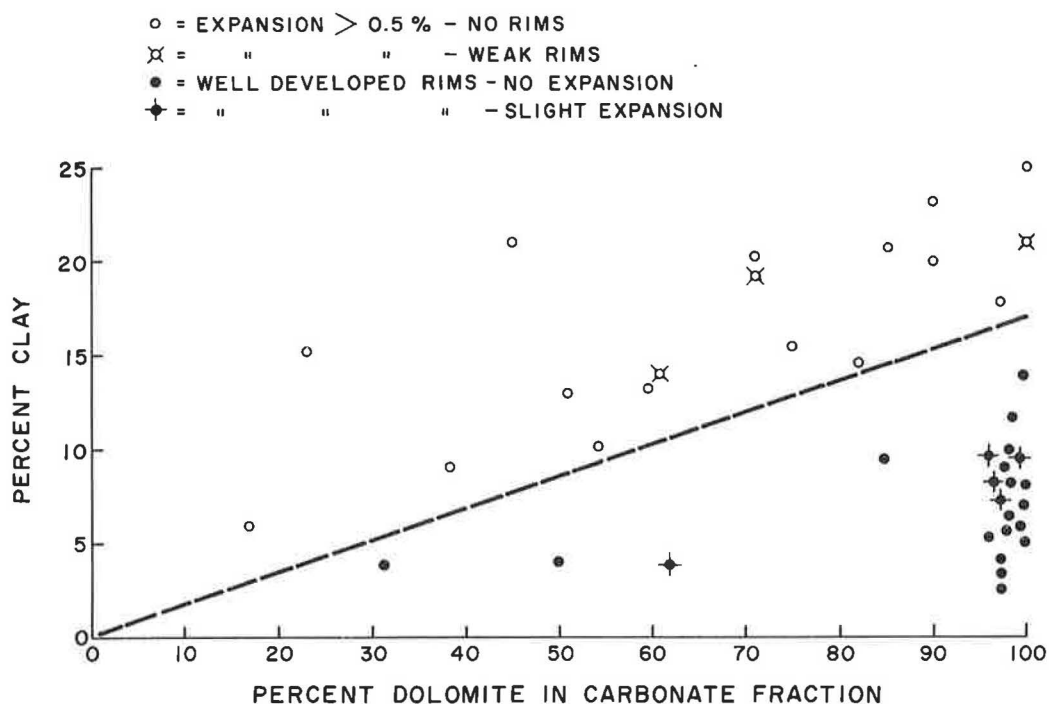


Figure 13. Rim development and expansion are closely related. Type of reactivity shown by a rock is a function of both clay content and carbonate composition.

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

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

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

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

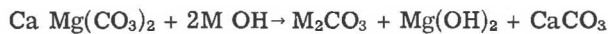
In rocks which contained more reactive calcite-dolomite mixtures and/or larger amounts of clay, the expansive forces are sufficiently strong to overcome the restraint of the carbonate skeleton and dedolomitization is accompanied by expansion of the rock

and a rapid disruption of the concrete. The same chemical processes are involved in both types of reactivity, and given sufficient time, the paste surrounding the expanding aggregate particles would be affected in the same manner as with rim-developing rocks. However, due to extremely rapid disruption of the concrete as a result of expansion of the aggregate, the carbonation of the paste would cease to be a significant factor.

### SUMMARY

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

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



in which M = Na, K, or Li.

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

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

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

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

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

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## *Appendix A*

### QUANTITATIVE CHEMICAL STUDY OF KINETICS OF DEDOLOMITIZATION REACTION

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

#### Materials

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

Percent by Weight			
	CaO	MgO	CO <sub>2</sub>
Dolomite	30.71	21.57	47.46
Calcite	55.21	00.24	43.78

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

Solutions of the alkali metal hydroxides were prepared taking every precaution to avoid carbonation. Fresh solutions were prepared for each experiment, and each

solution was analyzed for carbon dioxide. The  $\text{CO}_2$  (carbonate ion) content of most of these solutions was less than the minimum amount detectable (0.03 percent) by the analytical methods used. Only as much as 0.04 percent  $\text{CO}_2$  by weight was detected in isolated cases.

### Experimental Procedures

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

After 14 days the samples were filtered rapidly in a  $\text{CO}_2$ -free atmosphere. The filtrates were placed in small polyethylene bottles which were then sealed with wax pending analysis. Typical results are shown in Figures 5 and 6.

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

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

The determinations of the carbon dioxide contents of the alkali solutions were made by an evolution procedure. In the apparatus<sup>1</sup>, nitrogen gas is used to carry the  $\text{CO}_2$ , liberated by acid and heat, into a weighing tube containing ascarite and anhydrous magnesium perchlorate. Copper sulfate was not used in the train, and sulfide sulfur would interfere, if present. No accuracy was lost as the materials used did not contain sulfide.

### Accuracy of Determinations

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

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

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

## *Appendix B*

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

#### Introduction

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

#### Apparatus

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

Clay Membranes.—Raw Fithian illite, was air-dried and ground to pass a 200-mesh screen. Water was then added until the material was sufficiently plastic to be workable. The moist clay mass was sealed in a polyethylene bag and aged in the moist room for 14 days. The clay was then placed between two sheets of plastic film and rolled out with a rolling pin to a thickness of  $\frac{1}{2}$  in. A series of membranes 2 in. in diameter was cut from the sheet with a razor blade and stored over water in a sealed container until used.

Rock Membranes.—A series of rock membranes 2 in. in diameter and  $\frac{1}{2}$  in. thick were cut, using a diamond saw from a rock which was a very homogeneous argillaceous dolomitic limestone from the Mississinewa shale (Silurian) of Indiana. The rock contained 16 percent acid-insoluble residue, and 20 percent of the carbonate fraction was dolomite.

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

Test 1.—One chamber of the cell contained 1M NaOH, the other an equivalent amount of 0.5M NaCO<sub>3</sub> solution. This system represents the concentration relationships which would presumably be present in a reacting rock.

Results.—A very rapid flow took place into the side of the cell containing the NaCO<sub>3</sub> solution with both types of membrane.

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

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

#### CONCLUSION

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

## Discussion

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

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

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

TABLE 5  
CALCULATION OF AMOUNT DOLOMITE REACTED

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

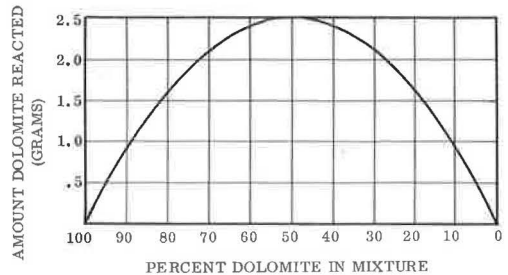


Figure 14. Amount dolomite reacted vs percent dolomite in mixture.