

Alkali Reactivity of Carbonate Rocks— Expansion and Dedolomitization

DAVID W. HADLEY, *Associate Research Geologist,
Applied Research Section, Research and Development Laboratories,
Portland Cement Association, Skokie, Ill.*

Although unsatisfactory performance of limestone and dolomite aggregates in concrete is relatively rare, certain carbonate rocks have been found to expand rapidly in solutions of the alkali metal hydroxides. These reactive rocks can be categorized on the basis of mineral composition and texture, all being argillaceous dolomitic limestones. In terms of texture, the rocks are best described as partially dolomitized calcilutites; that is, small dolomite crystals scattered through a matrix of extremely fine grained calcite and clay. A simple and rapid laboratory test for the expansive reaction in alkali has been developed.

The expansion of these rocks accompanies the following chemical reaction between the alkalies and the mineral dolomite:



where M stands for K, Na, or Li.

In concrete, the alkali carbonate produced in the dedolomitization reaction will react with hydrated cement products and the alkalies will be regenerated, permitting a continuing reaction with the dolomite.

The rates of both expansion and dedolomitization are functions of the calcite-dolomite ratio and texture of the rock. Although single crystals of dolomite will slowly dedolomitize and expand in alkaline solutions, maximum reaction occurs when calcite and dolomite are present in approximately equal amounts, and when both are extremely fine grained.

• IN RECENT years an extensive literature has been developed dealing with concrete failures in which limestone coarse aggregate was suspected as the causative factor. In 1945 Woods (1) correlated numerous cases of pavement disintegration in Indiana with a small number of aggregate sources. Slate (2) and Sweet (3) studied these rocks in great detail; although they could find no evidence of chemical reactivity, some of the suspected rocks were found to behave poorly under freezing-and-thawing conditions. Patton (4)

reported that these rocks were confined to narrow stratigraphic zones and were quite similar in lithology. In Iowa, Roy *et al* (5) described a limestone aggregate which had an extremely poor service record in spite of the fact that it passed the existing acceptance tests. Although no definite conclusions were reached regarding the cause of concrete disintegration, it was stated that the swelling of clay minerals within weathered rocks showing high absorptions might well be a factor.

In more recent work Bisque and

Lemish (6) studied another group of Iowa rocks and noted the presence of reaction rims on aggregate particles from affected concrete. They attributed these rims to the migration of silica from the cement paste to the aggregate. Another case of concrete failure attributable to the poor performance of a carbonate aggregate was reported by Swenson (7). In spite of its poor service record, this rock, which outcrops near Kingston, Ontario, easily passed all of the ASTM acceptance tests. An indication of a possible deleterious chemical reaction was found in the fact that the performance of the rock in concrete was a function of the alkali content of the cement used.

In summary, several instances of carbonate aggregates with poor service records have been reported. As determined by existing acceptance tests, most of these rocks were physically sound and all appeared to be chemically unreactive. In several cases, however, some as yet unrecognized form of chemical reactivity was suspected.

Work on these aggregates was undertaken at the Portland Cement Association Laboratories as part of a broad program of aggregate research, aimed at obtaining a better understanding of those physical and chemical factors which influence aggregate performance.

The general outline of this program is as follows:

Samples of Iowa and Kingston, Ontario, rocks having poor service records were studied to verify their expansivities in the presence of alkali using a specially developed but simple and rapid technique.

Chemical, optical and X-ray diffraction studies of the Iowa and Kingston rocks and of a special suite of several hundred other carbonate rocks showed the expansive aggregates to be argillaceous dolomitic limestone, containing approximately equal amounts of calcite and dolomite

together with appreciable quantities of clay and small amounts of reactive silica. It could not be demonstrated that the clay and silica fractions were involved in the expansive reaction. It was observed that the mineral dolomite was destroyed by reaction with alkali solutions forming brucite, calcite and alkali carbonate in solution. The rate of reaction and associated expansion was observed to depend significantly on the texture of the rock and on the calcite-dolomite ratio.

The chemistry and kinetics of the dedolomitization reaction were further studied by exposing artificial mixtures of calcite and dolomite to alkali solutions. The greatest total amount of dedolomitization was observed to occur in mixtures containing equal amounts of calcite and dolomite, similar to the greatest dedolomitization and expansion of carbonate rocks with such composition. Additional evidence of the interrelationship between dedolomitization and expansion was obtained by careful measurement of a single dolomite crystal which expanded 0.15 percent after 3 months in alkali.

Sample Suite

In addition to samples donated by the Illinois and Indiana state geological surveys, and the Canada Cement Co. and Dragon Cement Co., several hundred carbonate rocks were collected from Indiana, including many from stratigraphic zones known to contain rocks with poor service records as concrete aggregates. Because the major aim in collecting these samples was to incorporate as wide a mineralogical and textural range as possible, no attempt was made to confine the sampling to physically sound rock materials. A large proportion of the rocks collected, therefore, would undoubtedly be rejected as aggregate materials simply on the basis of their physical properties. Field experience with the Kingston aggre-

gate and similar materials indicates, however, that physically sound but alkali-reactive carbonate rocks do occur.

THE ALKALI-REACTIVE CARBONATE ROCKS

After it was determined that certain carbonate rocks were alkali-reactive, a need arose for the development of a simple test for the recognition of these reactive materials. Swenson (7) had already observed that cement-aggregate combinations with poor field performance showed abnormal expansion in concrete tests, even though such abnormal behavior was not revealed in the standard mortar bar test. Inasmuch as the reaction or reactions in question resulted in a measurable expansion in concrete, a test for this expansion in the rock itself seemed a most logical approach.

This approach proved most fruitful; a simple method of test was developed which appeared to distinguish between reactive and non-reactive rocks in the limited number of instances where information on field performance was available. Consequently, all rocks in the test series were tested for expansion in alkali. Inasmuch as the field data were very limited, the significance of this test has not been adequately verified. For the purposes of the present paper, therefore, the terms "reactive" and "non-reactive" refer specifically to the behavior of the rocks in the expansion test.

The details of the test method are as follows:

A. Test for Expansion

Procedure—Small prisms ($\frac{1}{4} \times \frac{1}{4} \times 1\frac{1}{4}$ in.) are cut from each rock with a diamond saw. Whenever possible, the prisms are cut perpendicular to the bedding. With the use of the small prisms the companion samples

required for the various tests to be performed (expansion, diffraction, microscopical, and chemical) can be selected from localized small zones in the gross aggregate specimen and hence are presumed to be most nearly similar. From a practical standpoint, the use of small prisms also makes it possible to test gravels, material from aggregate stockpiles and even coarse aggregate particles removed from concrete. Conical apices are ground on the prisms on a standard metalworking lathe and the prisms are immersed in water until constant length is attained.

The test pieces are then placed in individual polyethylene bottles containing 40 ml of 1M NaOH. When

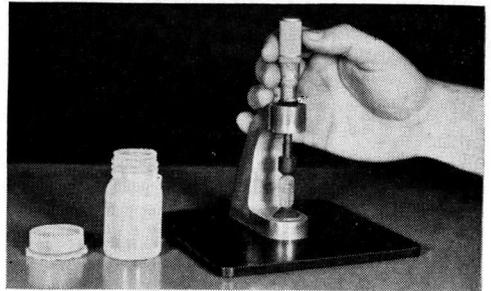


Figure 1. Simple test for measuring rock sample expansion produced in alkali solution.

measurements are desired, the prisms are removed from the bottles with forceps, rinsed in distilled water, and blotted dry. Measurements are made with the small comparator shown in Figure 1, which consists of a micrometer head mounted on an Invar steel yoke. After measurement, the prisms are immediately returned to the bottles and the bottles resealed.

Results—Certain of the Iowa, Ontario and Indiana carbonate rocks showed significant expansions after 14 days treatment in 1M NaOH solution. The prisms were allowed to react until expansion ceased. Final expansions in excess of $2\frac{1}{2}$ percent

were measured in some cases. In concurrent but separate research, Swenson and Gillott (8) also found that some beds of the Kingston material showed significant expansion in alkali.

B. Measurement of Expansive Force

The expansion of certain carbonate rocks in alkali need not be expected to correlate with the observed deterioration of concretes made with these materials unless it can be shown that the expansion is sufficiently forceful to disrupt a hardened paste. Therefore, an experiment was designed to measure the expansive force.

A prism of Kingston rock $1\frac{1}{2} \times 1\frac{1}{2} \times 3\frac{1}{2}$ in. was placed in a waxed container and mounted on a 20,000-lb testing machine. Gage points were mounted on the rock, and passed through rubber-dam ports in the sides of the container. The prism was then immersed in 1M NaOH and the force necessary to maintain constant length was determined. An expansive force of 2,180 psi was developed within seven days. This is certainly adequate to account for the observed concrete failures.

C. Determination of Mineralogical Parameters

In an effort to determine whether or not the rocks which had been found to be reactive could be categorized on the basis of their lithologic characteristics, the gross mineralogy of representative carbonate rocks was determined.

The acid-insoluble residue, clay composition and calcite-dolomite ratio were determined for each rock. The influence of rock texture and dolomite crystallinity was also evaluated.

Acid-Insoluble Residue—For each rock 100-gm samples were oven dried, ground to pass a 50-mesh screen, and treated with a 6N HCl

until reaction was completed. The residue was then washed free of salts, oven dried, the residue weighed, and the percentage of the original oven-dried weight calculated.

The amount of non-carbonate material contained by rocks in the test series ranged from almost nothing to more than 50 percent. However, those rocks which expanded in an alkali solution were all found to contain between 10 and 20 percent acid-insoluble residue, consisting largely of clay.

Clay Mineralogy—The acid separation of clay minerals from carbonate rocks is difficult, owing to the fact that some clays are readily altered by acid solutions (9). Ostrom (10) has studied this problem in detail and found the degree of alteration of the clays to be largely a function of the concentration of the acid used, and the duration of exposure to acid.

The method of separation adopted for this study is similar to that proposed by Ostrom. Finely ground carbonate is treated with only enough dilute acid to react with about 10 percent of the carbonate present. The rapid acid-carbonate reaction quickly neutralizes the acid and experiments show the damage to the clay fraction to be almost undetectable by X-ray diffraction techniques. The major difference in the two methods is that while Ostrom recommends the use of acetic acid with rocks in which the predominant carbonate is calcite, the writer preferred to use 3 percent HCl in all cases. It was felt that in a comparative study it was preferable to subject all samples to precisely the same treatment. When visible reaction between the acid and carbonate was complete the suspended material was decanted, washed free of chloride ion, and the clay minerals separated by conventional sedimentation techniques. In no case was it found necessary to use a dispersing agent, as two or three washings were usually sufficient to

disperse the clays. The clays were studied by X-ray diffraction using oriented-aggregate techniques in which the clay particles are allowed to sediment onto a glass slide. Because of the plate-like habit of most of the clay minerals, the particles tend to come to rest with the same orientation, which greatly enhances the intensity of the basal reflections. Untreated and glycolated slides were prepared for each clay and auxiliary heat treatments were employed when necessary for identification. When quantitative estimations of composition were deemed necessary, the method outlined by Johns *et al* (11) was used.

The dominant clay mineral in all samples studied was illite. All of the samples from Indiana and Iowa also contained relatively large amounts of a mixed-layer clay, which appeared to be a heterogeneous random mixture of 10Å and 14Å material. A small amount of chloritic material was present in the rocks from Ontario, and one of the Indiana samples contained a trace of kaolinite.

All of the rocks within each depositional area, reactive and non-reactive alike, contained comparable clay mineral assemblages. Quantitative studies showed that the relative abundance of mixed-layer material could not be correlated with reactivity in alkali. These data indicate that clay mineral composition is not a determining factor in the alkali reactivity of carbonate rocks.

Calcite-Dolomite Ratio—The relative abundance of calcite and dolomite in the rocks was determined using an adaptation of the methods of Tennant and Berger (12). The material used for the determination was cut from each rock immediately adjacent to the area from which the small test prism had been removed. The rock was ground in a vibratory ball mill until all material passed a 325-mesh screen, and was analyzed by X-ray diffraction techniques. The

ratio of the integrated intensities of the principal calcite and dolomite peaks was computed, and the percentage composition taken from Tennant and Berger's empirical plot.

Although the carbonate fraction in most of the samples in the test series contained less than 10 or more than 90 percent dolomite, the reactive rocks were found to be those of an intermediate composition with the most reactive samples containing from 40 to 60 percent dolomite in the carbonate fraction.

Textural Studies—All samples in the test series were also studied under the petrographic microscope using polished section techniques. It was found that all of the reactive carbonate rocks shared a common texture. Figure 2a shows the characteristic appearance of the reactive rocks. The matrix of the rock is composed of micro-crystalline calcite with abundant admixed clay material. Scattered randomly throughout the matrix are small rhombs of dolomite and occasional pieces of silt-sized quartz and feldspar. Pyrite, although not universally present, seems to be somewhat characteristic of rocks showing this texture.

In hand specimens, the reactive materials are lithographic to sub-lithographic and commonly display conchoidal fracture. Most of the reactive rocks are finely laminated.

Dolomite Composition and Crystallinity—Dolomite is normally considered to be a compound of magnesium and calcium carbonates in about an equal molar ratio. Goldsmith and Graf (13) report that in an ideal dolomite, the crystal is composed of a regular alternation of calcium and magnesium carbonate sheets. Naturally occurring dolomites may deviate from the ideal structure and composition through isomorphous substitution or by imperfect ordering of the calcium and magnesium components, or both. Because it has been suggested that the reactivity of certain

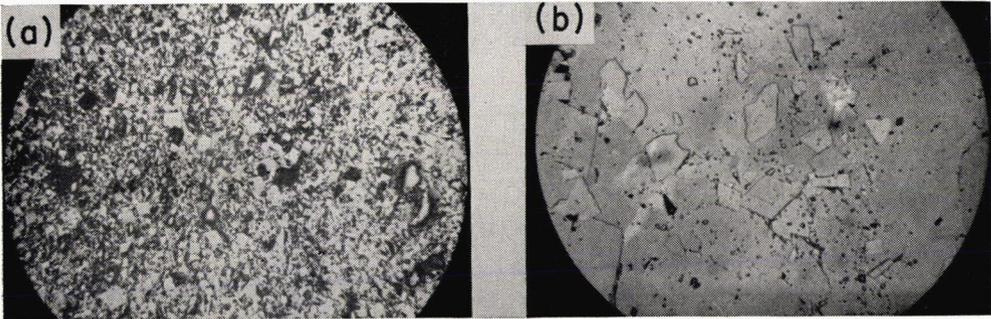


Figure 2. Influence of textured variations in dolomitic limestones. Reactive type (left) has small euhedral dolomite rhombs in fine-grained matrix of calcite and clay minerals; unreactive type (right) has comparatively larger grain size and coarsely crystalline calcite matrix.

dolomitic aggregates might be related to the presence of a non-ideal dolomite, the crystallinity of representative dolomites was investigated using the methods of Goldsmith and Graf.

The dolomite was concentrated, taking advantage of the greater solubility of calcite in dilute acids, and the difference in particle size between the carbonate and clay fractions. After treatment with dilute acid and subsequent sedimentation separations, the dolomite concentrate was examined by X-ray diffraction techniques. The intensity of the (11.0) reflection, which has no c-axis component and is not an order reflection, is relatively unaffected by variations in composition or the degree of ordering. It therefore can be used as a standard against which to compare the intensity of the (01.5), a principal ordering reflection. The ratio of the intensities of these two peaks thus serves as a measure of crystallinity.

All of the samples in the test series in which the dolomite occurred as euhedral crystals displayed a relatively high degree of crystal disorder. Thus, whereas all of the reactive rocks contained poorly crystallized dolomite, this feature was also present in many of the associated non-reactive rocks. Dolomite crystallin-

ity would therefore not seem to be an important factor in the alkali-carbonate reaction.

In summary of this portion of the paper, all of the reactive rocks were found to be argillaceous dolomitic limestones. Dolomite content ranged from 40 to 60 percent of the carbonate fraction. Although the type of clay present in the rock did not seem to affect the reactivity, all of the reactive rocks contained between 10 and 20 percent acid-insoluble residue, largely present as clay.

The reactive rocks also displayed a characteristic texture, all being partially dolomitized calcilitites. In polished sections, the reactive rocks were seen to be composed of small isolated dolomite rhombs, "floating" in a matrix of clay and micro-crystalline calcite.

NATURE OF THE REACTION

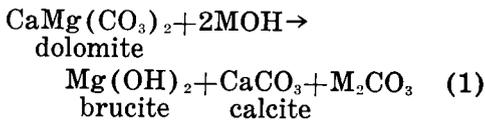
In an attempt to isolate the factors responsible for the observed expansion in alkali, the effect of alkali on the carbonate, clay and siliceous components of representative rocks was studied in some detail.

Although some of the rocks tested contained some form of alkali-soluble silica, no correlation was found between reactive silica content and the expansion in alkali. The expansion

therefore, did not seem to be due to the classical alkali-aggregate reaction. Both the clay and the calcium carbonate were found to be largely unaffected by alkaline treatment and were ruled out as primary factors. (It is possible, however, that slight expansions might be due to a change in the water sorption properties of the clay due to exchange phenomena or the removal of organic materials from the clay surfaces.) It was found, however, that the mineral dolomite entered into a chemical reaction with alkalis in solution.

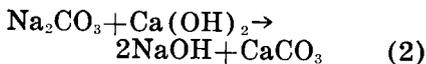
The Dedolomitization Reaction

The fact that the mineral dolomite is prone to enter into a chemical reaction with alkaline solutions has been recognized for some time. Chaiken and Halsted (14) mention the reaction in terms of carbonate interferences in the Quick Chemical Test (ASTM Designation C289). Stanton (15) reported that the chemical breakdown of magnesium carbonate in the siliceous magnesium limestone of California might play some part in the disintegration of concretes made with this aggregate. He later established that an alkali-silica reaction was the primary factor. The reaction between dolomite and the alkali metal hydroxides can be written as



in which M represents K, Na, or Li.

In concrete, the alkali carbonate produced in reaction (1) would react with the hydration products of portland cement; for example,



As reaction (2) regenerates the alkali, the dedolomitization reaction

would continue until the dolomite was completely reacted, or the alkali concentration was sufficiently reduced by secondary reactions.

Dedolomitization in Concrete

Early in the course of researches into the poor performance of Kingston aggregate, Swenson and Gillett (8) and the present writer found that the dedolomitization reaction took place when Kingston aggregate was treated with alkali solutions. X-ray examination of the treated rock showed both the disappearance of the dolomite and the presence of the reaction product brucite.

The following experiment was performed to determine whether the dedolomitization reaction was actually taking place in concrete made with Kingston aggregate.

A 2x2x6-in. prism of the Kingston limestone was equipped with metallic end plugs, centered on a standard metalworking lathe, and ground to a cylinder 1.3 in. in diameter. This cylinder was then centered in a cylindrical mold and cast in a 1-in. jacket of neat cement paste (0.5 water-cement ratio; cement alkali content, 0.06% Na₂O, 1.3% K₂O). Figure 3 shows the aggregate cylinder and mold. The sample was then moist cured for eight months, after which the specimen was again centered on the lathe, and a series of samples was turned off at regular intervals first through the paste and then through the aggregate.

X-ray analysis showed the rock to be strongly dedolomitized at the paste-aggregate interface, with the reaction becoming progressively less pronounced in the interior samples. Figure 4 shows the change in intensity ratio of the principal calcite and dolomite peaks as a function of distance from the paste-aggregate interface. The paste showed no alteration with the exception of that material immediately adjacent to the aggregate, which showed strong peaks

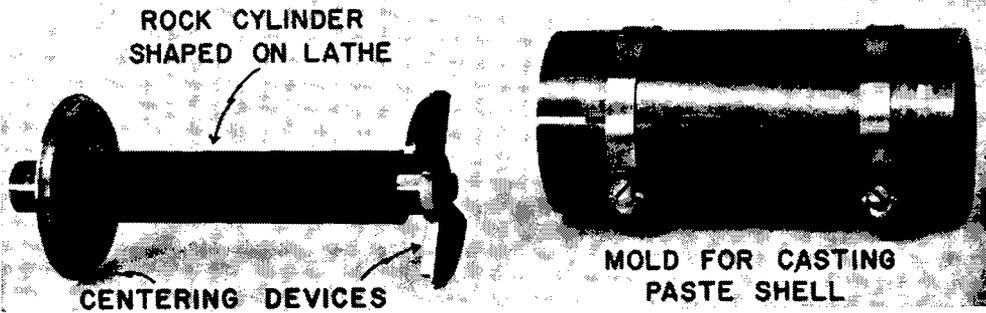


Figure 3. A cylinder of rock is embedded in a concentric cement paste shell for the study of chemical reactions at the paste-aggregate interface.

corresponding to calcium carboaluminate (Fig 5). This reaction can be attributed to the carbonate ion released as a by-product of the dedolomitization reaction.

Dedolomitization as the Mechanism for Expansion

Although it had been demonstrated that a chemical reaction was taking place between the reactive aggregates and cement alkalis, there was no

proof that the observed expansions were attributable to the dedolomitization reaction. A series of experiments was therefore designed to investigate this relationship, first by determining whether the two phenomena were both dependent on the same mineralogical and textural features, and second by investigating the dimensional stability of a single dolomite crystal subjected to dedolomitization by immersion in an alkaline solution.

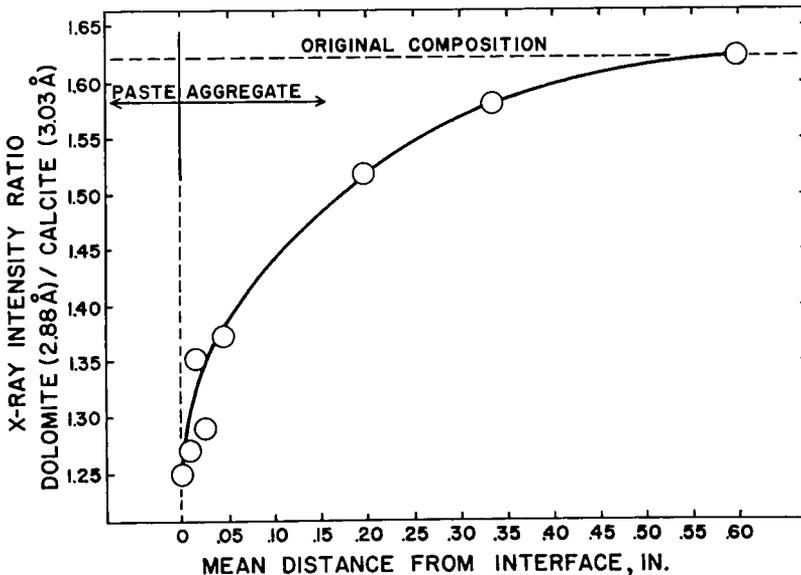


Figure 4. Dedolomitization of Kingston aggregate in high-alkali cement paste.

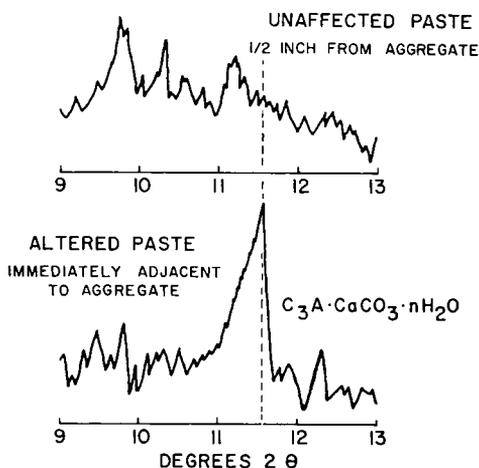


Figure 5. X-ray diffraction diagrams showing that paste immediately adjacent to Kingston aggregate has been carbonated.

Rate of Expansion—As previously stated, the most reactive carbonates were found to contain between 40 and 60 percent dolomite in the carbonate fraction. Inasmuch as reactivity appeared to be related to the mineral composition of the carbonate material, the available data were re-evaluated to determine whether the rate of expansion was also a function of carbonate composition. In Figure 6 the 14-day expansions of those rocks in the test series which were of intermediate composition are plotted against the carbonate composition of the rocks. Although the great majority of rocks in the test series showed no expansion, a definite relationship is seen to exist between the rate of expansion of the reactive rocks and the proportion of dolomite in the carbonate fraction. Maximum reactivity occurred in samples containing 50-50 mixtures of calcite and dolomite.

Rate of Dedolomitization—Following the recognition of dedolomitization in the Kingston limestone, a large number of dolomitic carbonate rocks were treated with alkali. The course of dedolomitization was

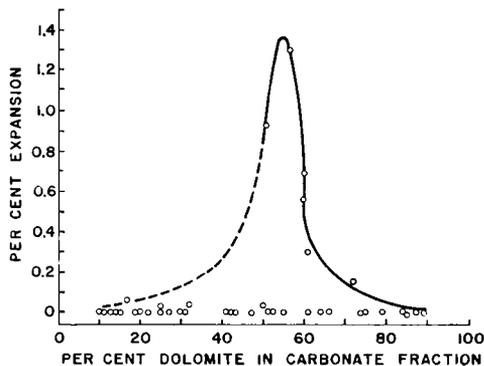


Figure 6. Alkali reactivity of carbonate rocks (measured by expansion after 14 days immersion in 1M NaOH solution) as a function of composition.

charted by periodic X-ray determination of the calcite-dolomite ratios. It was found that the rate at which the dolomite in a rock was destroyed was a definite function of the calcite-dolomite ratio of the rock. Figure 7 shows the relationship between initial dolomite content and the rate of

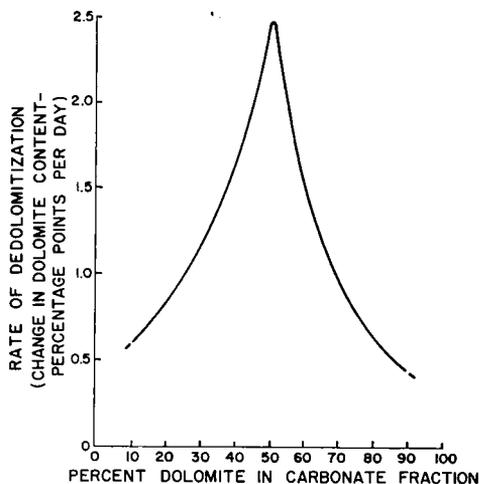


Figure 7. Rate of dedolomitization of carbonate rocks in 1M NaOH solution as a function of carbonate composition.

dedolomitization. In rocks containing more than 90 percent dolomite in the carbonate fraction, the rate of reaction was so slow that no detectable change had taken place after four months' exposure to alkali. Examination of Figures 6 and 7 shows that dedolomitization and expansion are both rate-dependent on the initial dolomite content of the rock, and the great similarity between the two curves would seem to indicate that the two phenomena are in some way related.

Influence of Texture—The apparent ambiguity in the carbonate composition-expansivity relationship is the result of the previously established influence of texture on reactivity. All of the expansive rocks display the texture shown in Figure 2a, whereas the non-expansive materials fall in other textural classes. Figure 2b shows a rock in which the carbonate fraction has a composition almost identical to that of the reactive rock shown in Fig. 2a, but which is non-expansive in alkali.

Although all of the rocks which contained intermediate amounts of dolomite reacted readily with alkali when finely ground, it was found that in unground samples the only rocks which showed any appreciable dolomite breakdown were those which displayed the texture shown in Figure 2a.

Expansion of Dolomite Crystal—The similarity of the influence of carbonate composition and texture on both expansion and dedolomitization made it seem likely that the two phenomena were related. To further substantiate this relationship it was decided to determine whether or not a single crystal of dolomite would measurably expand when treated with alkaline solutions.

A crystal of dolomite from Traversella, Italy, donated by Albert W. Forslev of the Chicago Natural History Museum, was mounted in the apparatus shown in Figure 8. The

crystal was immersed in 3M NaOH and expansions were measured normal to a rhombohedral face using a Monfore standardizing strain gage (16).

The dolomite rhomb expanded approximately 0.15 percent after 100 days. As chemical kinetics studies soon to be published have shown that reaction of pure dolomite is extremely slow, even when finely ground, the expansion shown by the relatively large dolomite rhomb (approximately 0.3-in. gage length) is surprisingly great. It would seem that the expansion of the dedolimitizing crystals themselves would be sufficient to account for the expansion of the reactive carbonate rocks.

Additional Factors Influencing Expansion of Reactive Aggregates

1. *Hydroxide Concentration*—Because the expansion of concrete made with Kingston aggregate was a function of the alkali content of the cement, an experiment was performed to determine the influence of variations in alkali hydroxide concentration on the expansion of Kingston

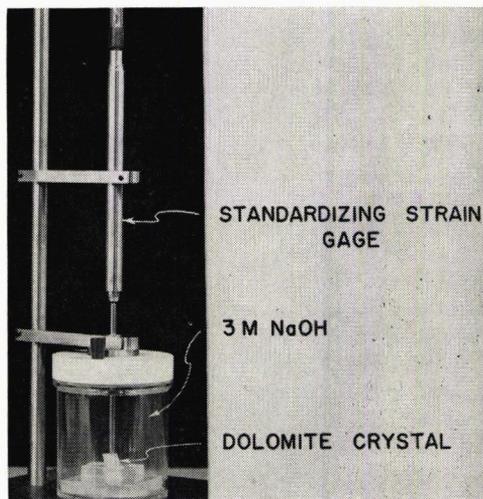


Figure 8. Apparatus used for measuring the expansion of a single dolomite crystal.

rock. The results are given in Table 1. Although the rate of expansion in solutions of 0.5 M or greater is proportional to the concentration, final measurements show the total expansions to be approximately equal.

2. Ionic Species—To determine whether the expansion of reactive carbonates was also a function of the particular alkali hydroxide used, samples of Kingston rock were exposed to solutions of sodium, potassium and lithium hydroxide, prepared to be of equal activity. The results (Table 2) show that both the rate of expansion and the total expansion are a function of the alkali ion present.

Chemical Studies

Extensive research is being carried out on the chemical kinetics of the dedolomitization reaction and early experiments have thrown some light on the manner in which variation in carbonate composition and grain size affect the rate of reaction. The results of these experiments will be published in full when research is completed.

Procedure—Five-gram samples of various proportions of calcite and dolomite, ground to various degrees of fineness, were reacted with 20 ml of 1M NaOH solution in individual plastic bottles. After 14 days the mixtures were filtered and the filtrates analyzed for CO_2 in solution.

Results—Figure 9 shows the relationship between the weight of dolomite reacted and the initial calcite-dolomite ratio for 200-400 mesh calcite and dolomite after 14 days in 1M NaOH. Comparison with Figure 6, which was derived from X-ray diffraction studies of the dedolomitization of natural rock samples, shows the two curves to be quite similar. In Figure 10, the data are replotted with the dedolomitization expressed in terms of the percentage of initial

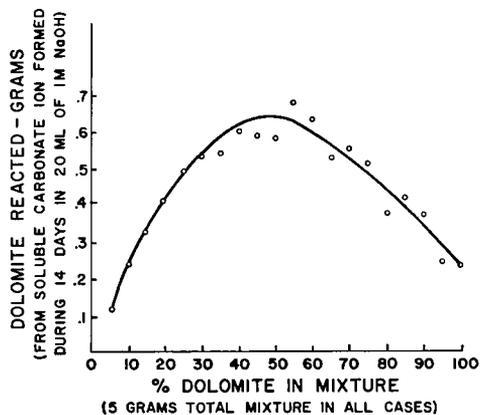


Figure 9. Effect of calcite-dolomite ratio on dedolomitization of laboratory mixtures of calcite and dolomite.

dolomite reacted. From this plot, it can be seen that the rate of reaction is a direct function of the amount of admixed calcite. Additional experiments have shown that the rate of reaction is also dependent on the surface area of the admixed calcite. Figure 11 shows the effect of variation in calcite grain size.

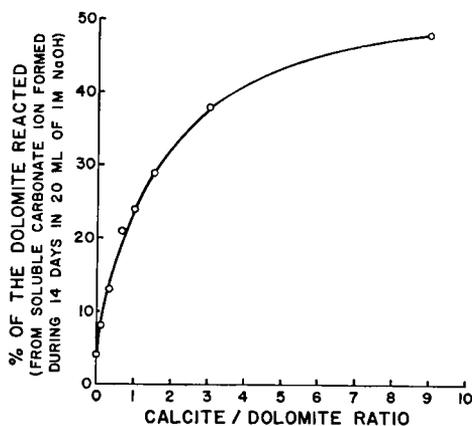


Figure 10. Accelerating effect of admixed calcite on dedolomitization in laboratory mixtures.

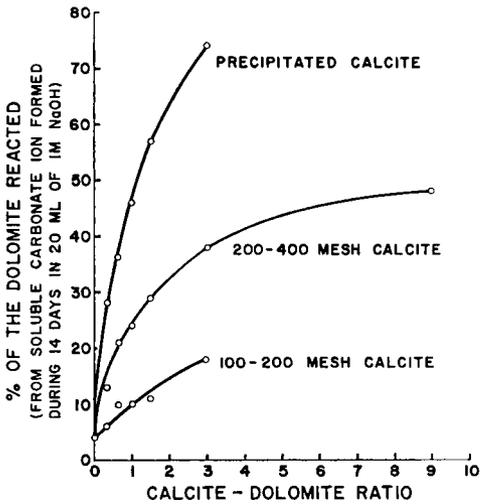


Figure 11. Effect of calcite grain size on dedolomitization in laboratory mixtures containing 200 to 400-mesh dolomite.

SUMMARY

Although the great majority of carbonate rocks are not reactive, certain carbonate rocks have been shown to react and expand rapidly in alkali solution. The reactive rocks can be categorized as follows:

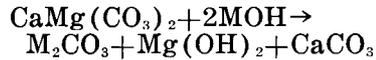
Texture—Partially dolomitized calcilutites; small, isolated dolomite rhombs in a matrix of micro-crystalline calcite and clay.

Carbonate Mineralogy—Dolomitic limestone; dolomite comprises from 40 to 60 percent of the carbonate fraction. Crystallinity of the dolomite does not appear to be an important factor.

Clay Mineralogy—Rocks contain between 10 and 20 percent clay. All samples were primarily illite, but clay composition does not appear to be critical.

Treatment of the reactive rocks

with alkalis was found to produce the following chemical reaction:



in which M represents K, Na, or Li.

The rates of both expansion and dedolomitization are functions of the calcite-dolomite ratio and texture of the rock. Maximum reaction occurs when calcite and dolomite are present in approximately equal amounts, and when both are extremely fine grained.

It has been shown that the expansion of the reactive rocks accompanies the expansion of the dedolimiting crystals themselves.

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