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MECHANISM AND KINETICS OF EXPANSION IN THE
ALKALI-CARBONATE ROCK REACTION

BY

J. E. GILLOTT

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SOMMAIRE

Les parties solides de certaines pierres à chaux argileuses et dolomitiques et à fine granulation augmentent de volume lorsqu'on les place dans un alcali fort. Une analyse minéralogique montre que la dolomite est remplacée par de l'hydrate de magnésium (brucite), du carbonate de calcium et du carbonate d'alcali. Cette réaction n'est pas directement responsable de l'expansion car le volume des produits solides est inférieur au volume de la dolomite.

On montre que l'accroissement volumétrique des parties solides est dû à une absorption d'eau. Ce comportement est expliqué par une hypothèse qui peut être résumée comme suit:

(1) L'attaque de l'alcali sur des cristaux dolomitiques émet de l'argile, déjà présente, à l'état "actif" avec une surface non humide.

(2) Quelques-uns des ions Ca^{++} et Mg^{++} probablement présents dans les zones d'échange sont remplacés par des ions Na^+ .

(3) Il se développe une double couche hydratée formée de molécules d'eau orientées, les cations étant près de la surface d'argile nouvellement exposée et les anions plus éloignés de cette surface.

(4) Le développement de la double couche et les processus d'hydratation concomitants provoquent l'absorption de l'eau qui conduit à l'accroissement volumétrique.

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MECHANISM AND KINETICS OF EXPANSION IN THE ALKALI-CARBONATE ROCK REACTION¹

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ABSTRACT

Certain fine-grained argillaceous dolomitic limestones show an increase in solid volume when placed in strong alkali. Mineralogical analysis shows that the dolomite is replaced by magnesium hydroxide (brucite), calcium carbonate, and alkali carbonate. This reaction does not account directly for the expansion, as the volume of the solid products is less than the volume of the dolomite.

Expansion is shown to be the result of an increase in solid volume that results from water uptake. The behavior is accounted for by a hypothesis that may be summarized as follows.

- (1) Alkaline attack on the dolomite crystals releases included clay in an "active" state with an unwetted surface.
- (2) Some of the Ca^{++} and Mg^{++} ions probably present on exchange sites are replaced by Na^+ ions.
- (3) Development of a hydrated double layer made up of oriented water molecules, cations near the newly exposed clay surface, and anions further from the surface.
- (4) Development of the double layer and accompanying hydration processes cause the water uptake, which leads to expansion.

INTRODUCTORY STATEMENT

Dolomite reacts with strong alkali to produce brucite (magnesium hydroxide), calcium carbonate, and alkali carbonate. Rocks in which this reaction occurs are said to undergo dedolomitization. Calculation shows that the molar volume of $\text{Mg}(\text{OH})_2$ plus that of CaCO_3 is less than the molar volume of dolomite. As the alkali carbonate will probably pass into solution no increase of solid volume is expected. Expansion does, however, accompany the dedolomitization of certain argillaceous dolomitic limestones. This type of rock is found at Kingston, Ontario; its petrology has been described (Gillott 1963a). The rock is physically sound according to the usual acceptance tests (Swenson and Legget 1960) and has been used as aggregate in concrete; but when combined with high alkali cement the aggregate expands and causes the concrete to crack and deteriorate. Rock that causes such expansion is commonly referred to as "reactive rock." Rock apparently similar to that from Kingston is now known to occur in Illinois and Indiana (Hadley 1961), Virginia (Newlon and Sherwood 1962), and South Dakota (Buck 1962). A different but related phenomenon is also known from Iowa (Lemish, Rush, and Hiltrop 1958; Bisque and Lemish 1958).

As it is not possible to account readily for the mechanism whereby the volume of the solid increases, the reaction is of scientific interest. The major importance of concrete as a construction material also gives it a special significance for engineers. At Kingston reactive limestone occurs in the major quarries that

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supply aggregate for concrete, so that its considerable economic significance makes it of special importance.

Several methods have been used to measure expansion of concrete and of rock which has been treated in alkali (Swenson and Gillott 1960; Hadley 1961; and Buck 1962). The volume change that results from action of strong alkali on powders was measured by means of two types of apparatus. One has been described (Gillott 1963*b*) and will be referred to as the "cell." The other will be referred to as the "dilatometer." The cell is designed to register only changes in the solid volume; the dilatometer registers volume changes of the whole system, solid and liquid. The results of volume change measurement obtained by use of the cell are therefore complemented by results obtained with the dilatometer.

Many dolomitic limestones do not expand when used as aggregate nor when powdered and tested in the cell. This suggests that the action of alkali on dolomitic limestone results in an increase in the volume of the solid only when the rock incorporates both the requisite texture and the appropriate composition. The scale of the various textural components in the rock fabric is known from microscopic observation, so that it was possible to predict the particle size range at which different textural elements would suffer severe damage from grinding. The extreme case was represented by mixtures identical in composition with reactive rock but texturally quite different. The effect of these textural changes on reactivity was evaluated by means of the cell.

All samples which contained finely ground dolomite registered expansion in 2 *M* NaOH when tested in the dilatometer.

As powder was used it was possible to follow the expansion smoothly to completion in a relatively short time. The rate of dedolomitization was followed by X-ray diffraction and differential thermal analysis and compared with the rate of expansion.

The mechanism is reviewed and a hypothesis is proposed to account for the expansion.

EXPERIMENTAL TECHNIQUES

In rate studies use was made of either four cells or four dilatometers assembled simultaneously and then dismantled after successive time intervals. This gave adequate sampling of the mineralogical and chemical changes that occurred during expansion. Mineralogical analyses were carried out by X-ray diffraction and differential thermal techniques. The alkaline solutions were chemically analyzed.

Sample Treatment

Rock crushed for use as aggregate was sampled representatively by means of a splitter. The crushed rock was ground to pass U.S. Standard sieves. Samples intended for subsequent quantitative analysis by X-ray diffractometry were ground to pass a 325-mesh sieve and then pulverized in a vibratory ball mill (Forziati and others 1950) in 2-g portions for periods of $\frac{1}{2}$ hour.

Mixtures of composition similar to that of reactive rock were prepared.

Almost pure dolomite was obtained from Florida and Massachusetts (Wards Mineral Suppliers). The dolomite from Florida is similar in composition to that in the Kingston rock; it is metastable protodolomite which contains an excess of calcium above the ideal 50 mole % (Goldsmith and Graf 1958). Massachusetts dolomite is close to the theoretical ideal composition for this mineral. Crushed Georgia White marble was used as a source of calcite. In some experiments chemically precipitated CaCO_3 was employed. The acid-insoluble fraction of the reactive rock was separated by means of either dilute acetic acid or dilute hydrochloric acid. After washing them with distilled water the clay minerals were flocculated with CaCl_2 . Illite is the dominant clay mineral with lesser amounts of chlorite (Gillott 1963a).

The constituents were mixed in appropriate proportions, homogenized as a slurry, dried, and mixed in a laboratory shaker to eliminate any fractionation that might have occurred during drying of the slurry. The mixtures were reduced to the same particle size as was the rock by use of the same grinding procedure. The same ball mill was used throughout.

When either a cell or a dilatometer was dismantled a sample of alkali was removed for titration. The cell can be separated into two halves to permit the powder to be removed as a compact. As the dilatometer has a narrow neck a suspension was shaken up and poured from the dilatometer. The powder was recovered by vacuum filtration. A known proportion of the solid was washed by repeated centrifugation with distilled water until no precipitate formed on addition of CaCl_2 . The washings were titrated. The solid was analyzed by quantitative X-ray diffractometry, X-ray powder photographs, and differential thermal analysis. Prior to use in the cell or dilatometer some samples of reactive rock and mixture were pretreated with surface-active agents.

Volume Change Measurement

In the cell the powder was confined under 5 p.s.i. air pressure in a compression chamber between a porous plate of stainless steel and a rubber membrane. The chamber below the membrane was filled with water and volume change was registered by the meniscus in a precision bore capillary tube. The powder communicated via the porous plate with a reservoir containing water. This was replaced by alkali when the system had reached equilibrium.

The dilatometer consists of a glass bulb of about 100-ml capacity connected by a ground glass joint to a precision-bore capillary tube. The weighed quantity of powder was placed in the bulb and evacuated to 10^{-3} mm mercury, when degassed 2 M NaOH was admitted. The dilatometer was chilled in ice so that the solution contracted and made room for a small addition of alkali. The capillary tube was then connected to the bulb and the dilatometer was placed in a water bath held at 22 °C. The attainment of water-bath temperature was accompanied by expansion of the alkali into the precision-bore capillary tube.

The cell differs from the dilatometer principally in that the reservoir is external to the compression chamber containing the sample. Only those volume changes that occurred within the compression chamber were recorded. In the

dilatometer the volume measured was that of the entire system—powder plus alkali. Hence, an uptake of moisture by the sample registered as a volume increase in the cell, but the same moisture movement in the dilatometer registered as a volume increase only if accompanied by a density decrease. Increase in volume of the solution registered as expansion only in the dilatometer and not in the cell. Study of identical samples in both cell and dilatometer made it possible to differentiate volume change in the solid from volume change in the solution.

In a later modification to the cell a length of precision-bore capillary tube was connected to the cell reservoir. This chamber was sealed by a cap and O-ring. By this arrangement moisture movement between reservoir and compression chamber and volume change within the solution were detectable.

X-Ray Diffraction Procedure

Powder taken from both the cell and the dilatometer was analyzed by X-ray diffraction, the pattern being recorded photographically with a Nonius Guinier quadruple-focusing camera and by a Hilger diffractometer employing scintillation counters and pulse height analysis. Copper radiation was employed, generated by a Hilger microfocus X-ray set.

The powder photographs were used for mineral identification. Each photograph taken with the Nonius Guinier camera can display four separate diffraction patterns. In rate studies a sample from each of the four cells dismantled during the 2-week experiment was X-rayed and the four diffraction patterns were recorded simultaneously on one film. This facilitated convenient visual comparison. Strip-chart recordings were made with the diffractometer and used for quantitative analysis of the carbonates. The theory and practice of the quantitative analysis of powdered mixtures by X-ray diffraction has been described (Klug and Alexander 1954; Copeland and Bragg 1958*a*; Brindley 1961; and Norrish and Taylor 1962). Weber and Smith (1961) and Tennant and Berger (1957) used an X-ray diffraction method to obtain satisfactory estimates of the dolomite to calcite ratio in the carbonate fraction of rocks. This method was employed in the present work and the precision was evaluated according to statistical procedures described by Shaw and Bankier (1954). The method involves preparation of a calibration curve showing composition plotted against the intensity ratio of the strongest dolomite to the strongest calcite reflection. The standard mixtures from which the calibration curve was plotted were made up from Massachusetts dolomite and crystals of Iceland spar. The solid was ground to pass a 325-mesh sieve and then pulverized in the vibratory ball-mill in 2-g portions for $\frac{1}{2}$ -hour periods. This procedure reduced crystallites to about $2\ \mu$ diameter and minimized the probable error in the intensity of reflections (Copeland and Bragg 1958*b*). Use was made of a spinning specimen holder (de Wolff, Taylor, and Parrish 1959) modified to take an aluminum disk which was filled from behind (Klug and Alexander 1954). The powder was compacted at a constant pressure by a hydraulic press. A scanning speed was employed of $\frac{1}{16}$ deg 2θ per minute over the two principal carbonate

peaks, and areas were determined with a planimeter. Six analyses were performed on each sample, a separate disk being made up for each analysis.

A measure of the mean size of brucite crystallites was obtained from the half peak breadths of X-ray reflections from the $10\bar{1}1$ and 0001 crystallographic planes. The profile of each diffraction peak was determined by the fixed count technique, using an interval step of $1 \text{ min arc } 2\theta$. The Hilger diffractometer is equipped with two detectors, one of which monitors the X-ray beam incident upon the sample while the other receives the diffracted beam. The monitor scaler was set to record 10^4 counts at each step; the corresponding count diffracted by the sample was automatically recorded by the print-out unit. The profile of the powder line reflected by the $11\bar{2}0$ plane and the $10\bar{1}0$ plane of quartz was similarly recorded and used as a measure of the instrumental broadening. A single quartz crystal was ground and the powder sized in the 5- to $20\text{-}\mu$ range by sedimentation.

Klug and Alexander (1954) discuss the criteria that determine the precision of a crystallite size determination by this method. Best results are given under conditions that make the instrumental contribution to broadening as small as possible. If only slight broadening is present in the unknown peak, the precision also will probably be low, no matter what experimental conditions are adopted. The two brucite reflections used were not good from the experimental viewpoint, but were chosen because other peaks were either very weak or clashed with reflections from other phases in the sample. Owing to unfavorable conditions the pure diffraction profile of the $\text{Mg}(\text{OH})_2$ peaks was derived with the greatest accuracy by the Fourier transform procedure of Stokes (1948). In some instances values were also derived by the method introduced by Jones (1938).

Differential Thermal Analysis

Samples removed from the cell or dilatometer were air-dried and examined by differential thermal analysis. Some alkali and alkali salts were present in this material. Washed samples were also analyzed. A heating rate of 10°C per minute was employed; sensitivity was $50 \mu\text{volts}$. Samples were analyzed in CO_2 as dynamic gas under 45 p.s.i. by using the differential thermal analysis apparatus of R. L. Stone and Co.

Chemical Analyses

In rate studies a sample of 10 ml of alkali was taken from the dilatometer on dismantling. This was diluted to 200 ml to give an approximately $N/10$ solution for titration against standard HCl. Concentration of NaOH and Na_2CO_3 was determined by the method of Winkler (Treadwell and Hall 1951). The total Na_2CO_3 was obtained by combining the concentration for Na_2CO_3 in the solution with that found by titrating the washings from a known weight of the solid.

Porosity and Pore-Size Distribution

Some samples were examined in a mercury porosimeter capable of a maximum pressure of 50 000 p.s.i. at which pores of $20 \text{ \AA}$ radius are entered. The

technique was adapted from that described by Ritter and Drake (1945) and the work was carried out jointly with the Mines Branch of the Department of Mines and Technical Surveys (Canada) where the high pressure equipment was available.

EXPERIMENTAL RESULTS

Results of Volume Change Measurement

Results were plotted graphically with volume change as ordinate versus time as abscissa. Graphs showing a volume increase had the form of a fairly typical rate-curve in which an early rapid expansion tapered off asymptotically towards parallelism with the time axis (Gillott 1963*b*). Ball-milled samples produced expansion for about 2 weeks. Coarser samples expanded for longer periods.

The curve obtained when the cell was used has been described (Gillott 1963*b*). The first part of the curve resulted from compaction of the powder until an equilibrium was established. The water in the reservoir was then replaced by alkali. Commonly the meniscus registered a sharp contraction, which continued for up to 4 days, depending on the particle size of the sample. The contraction was attributed either to migration of water from between the particles of powder into the reservoir or to a change in structure within the powder-water system. After expansion had ceased in reactive samples the curve frequently had a greater downward slope than it had during the period when equilibrium had been attained prior to addition of alkali. This was attributed to an osmotic flow of water through the rubber membrane from below. Results obtained by use of the dilatometer gave graphs which were less complicated because of the simpler setup. Changes in packing of the powder did not register, and as no membrane was used osmotic effects were eliminated.

Results with Dilatometer

Samples tested in the dilatometer showed variation in the amount, rate, and degree of expansion that depend upon dolomite content, crystallite size, and strength of the alkali. When strength of alkali and particle size are constant those samples that produce the greatest expansion also contain the most dolomite.

When tested in 2 *M* NaOH in the dilatometer a ball-milled composite sample of the top 24 ft of a quarry near Kingston registered a volume increase of 1.17%, expressed as a percentage of initial solid volume. A ball-milled sample from a bed at a depth of 6 to 7 ft in the same quarry produced an increase in volume of 1.89%, similarly expressed. A ball-milled sample of a mixture that simulated the composition of the Kingston 6- to 7-ft sample produced a similar amount of expansion. The form of the rate-curve was also similar (Fig. 1).

Ball-milled samples of Florida and Massachusetts dolomite produced a volume increase of about 2.9 and 2.3%, respectively, when tested in the dilatometer in 2 *M* NaOH. In these tests some dolomite remained after expansion had apparently ceased. Samples of the same total weight, in which half the dolomite was replaced by CaCO₃, produced more than half the volume increase registered by the pure dolomite. A fall in the strength of NaOH accompanies

FIG. 1. Expansion in dilatometers in approximately 2 M NaOH.

the destruction of dolomite, and it is probable that exhaustion of NaOH limited expansion when pure dolomite was tested. Ball-milled Massachusetts dolomite was tested in 0.5 M NaOH. Expansion became very slow after 6 or 7 days and the total volume increase registered was only 0.35% of solid volume at 19 days. The strength of the solution with respect to NaOH was reduced from 0.4870 N to 0.0328 N. The reduced total expansion, which resulted from a decrease in strength of the alkali, is also illustrated by ball-milled samples of dolomite rock from Virginia (Fig. 2).

Massachusetts dolomite, which passed a 100-mesh sieve and was retained on a 200-mesh sieve, registered no expansion and only slight dedolomitization after 5 weeks in 2 M NaOH. A similar sample of Florida dolomite gave the same result. The reduction in rate of expansion resulting from increased coarseness of crystallite size was also observed in other dolomitic samples including those from Kingston (Fig. 1).

FIG. 2. Expansion in dilatometers of Virginia dolomitic limestone. Samples ground to pass through 325-mesh sieve prior to $\frac{1}{2}$ hour in vibratory ball-mill in 2-g portions.

A ball-milled sample of Georgia White marble and a sample of the acid-insoluble fraction of the Kingston reactive rock registered no expansion in 2 M NaOH when tested in the dilatometer.

Results with Cell

Samples of Kingston rock registered expansion in the cell greater than that registered in the dilatometer. The Kingston 0- to 24-ft material produced a volume increase of 7.79% of initial solid volume (1.17% in dilatometer—see above). A ball-milled sample of the Kingston 6- to 7-ft material from the same quarry increased its volume by 3.40% (1.89% in the dilatometer).

In the cell the total expansion registered by Kingston material varied with the particle size. Finer samples expanded sooner after alkali was supplied, but coarser samples produced the greatest total expansion (Fig. 3).

Samples of dolomite similar to those tested in the dilatometer and various mixtures were also investigated by means of the cell technique. The mixtures were made up to simulate the composition of the Kingston 6- to 7-ft rock. One mixture consisted of dolomite and a powdered limestone known to contain acid-insoluble minerals similar to those in the reactive Kingston rocks. Other

FIG. 3. Expansion in cells of Kingston 6- to 7-ft rock ground to different particle sizes.

mixtures were made from Florida and Massachusetts dolomite by mixing these separately with the acid-insoluble fraction of the Kingston rock, together with various samples of CaCO_3 . Ball-milled Georgia White marble, with a particle size of about $2\ \mu$, was employed as well as a commercial chemically precipitated form of CaCO_3 having a particle size range of about 0.04 to $0.3\ \mu$. None of these samples registered expansion in the cell (Fig. 4).

FIG. 4. Behavior in cells of samples used for rate studies.

Experiments were performed with the cell modified to incorporate a capillary tube connected to the reservoir in addition to the one connected to the compression chamber. Results for a sample of Kingston 6- to 7-ft material and a sample of the compositionally similar mixture are shown in Fig. 5. When the water in the cell reservoir was replaced by 2 M NaOH the movement of the meniscus in the reservoir capillary mirrored the movement of the meniscus in the capillary connected to the compression chamber. A decrease in the volume of solution in the reservoir was indicated for the Kingston 6- to 7-ft sample; in contrast an increase in the volume of solution in the reservoir was indicated for the mixture.

FIG. 5. Cell test using capillary tube in both reservoir and compression chamber.

Samples pretreated with various surface-active agents were also tested. One such surfactant available commercially consists of a mixture of unsaturated and saturated long-chain fatty acids. This product, which contains over 70% oleic acid, was used in several dilutions in an organic solvent as a pretreatment for samples of ball-milled Kingston 6- to 7-ft rock. A sample treated with the fatty acids in a dilution of 10% registered no expansion in the cell after 2 months' exposure to alkali. A sample treated in a 5% solution did not register expansion for 2 weeks after alkali had been supplied to the system. This cell was dismantled for X-ray analysis (of the powder), which showed that some dedolomitization had occurred; the dolomite content expressed as a percentage of the carbonate fraction was reduced from $44.6 \pm 1.2\%$ to $40.5 \pm 1.37\%$. A sample treated in a 1% solution of fatty acids did expand when tested in the cell, but the volume increase was unusually small and terminated after about 7 days instead of after 14 days as occurred with untreated samples. X-Ray analysis after 14 days in 2 M alkali showed that dedolomitization was also much less than normal; the dolomite content was 33.7 ± 2.21 expressed as a percentage of the carbonate. A similarly treated sample did not register expansion when tested in the dilatometer, although one sample treated in a 0.1% solution of the long-chain fatty acids registered a reduced rate of expansion.

Results of X-Ray Diffraction

Qualitative Analysis

A Nonius Guinier quadruple-focusing camera was employed to take powder photographs, which showed that dolomite is gradually destroyed by the action of the NaOH. Magnesium hydroxide was identified as a reaction product and on some films weak lines were attributed to $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

Quantitative Analysis

Decrease in dolomite content with time in NaOH was shown by samples removed from the cell or dilatometer. Rate studies of ball-milled samples showed that dedolomitization is more rapid for the Kingston 6- to 7-ft material than for the mineralogically similar mixture (Fig. 6). This difference in rate was particularly large in the early part of the test. A composite sample of Kingston material in which there was a lower initial dolomite content behaved similarly.

Error could arise in the results if some phase formed in the reaction produced an X-ray reflection that clashed with either of the two lines used for the analysis. If the dolomite line was enhanced there would appear to be more dolomite than was actually present and dedolomitization would seem slow; if the calcite line was enhanced an erroneously low dolomite content would be deduced and dedolomitization would seem fast. A comparison was therefore made between other lines on the diffraction patterns of the Kingston material and the mixture; this confirmed more rapid dedolomitization in the Kingston material than in the mixture.

After 14 days in 2 M NaOH the Kingston material contained less than 5% dolomite in the carbonate fraction. For all samples there was a slightly higher

FIG. 6. Rate of dedolomitization in cells based on X-ray diffraction.

rate of dedolomitization in the dilatometer than in the cell, probably because alkali was admitted under vacuum to the sample in the dilatometer. Powder in the cell was wet when alkali was supplied to the system, resulting in some dilution (Table I).

TABLE I
Kinetics of dedolomitization in dilatometers

Time in 2 M NaOH (days)	% dolomite in carbonate fraction based on X-ray diffraction*	% dolomite in carbonate fraction based on chemical analysis of Na_2CO_3
Mixture compositionally similar to Kingston 6- to 7-ft		
Initial	43.5 ± 1.22	—
2	35.75 ± 1.19	38.08
7	23.0 ± 1.24	26.48
14	8.0 ± 1.33	11.29
16	6.4 ± 1.34	6.66
Kingston 6- to 7-ft		
Initial	43.6 ± 1.20	—
2	24.25 ± 1.21	36.76
7	10.7 ± 1.29	22.61
14	5.6 ± 1.34	3.98
16	None detected	Nil

*Value expressed at 95% confidence level.

Line Profile Analysis

The dedolomitization reaction produced magnesium hydroxide, the X-ray powder lines of which showed only slight broadening. There was no systematic change in the half-peak breadth of the powder lines of the $\text{Mg}(\text{OH})_2$ in samples analyzed after increasing time in NaOH. Results indicated a mean crystallite

size of about 1 000 Å but precision was low because the broadening was slight. Crystals developed early in the reaction were apparently similar in size to those formed towards completion of dedolomitization. The brucite crystals had dimensions close to the upper limit of the colloidal state (Glasstone 1948). Results for the mixture were similar to those obtained for the Kingston samples.

Results of Differential Thermal Analysis

Unwashed air-dried material removed from the cells and dilatometers gave complex thermograms owing to the presence of alkali salts. The curves will not be described in this paper as kinetic effects were obscured. The progress of the dedolomitization reaction was followed by differential thermal analysis of samples washed free of alkali.

Thermograms of samples of Kingston material and of the mixture are shown in Figs. 7, 8, and 9. In each the topmost curve is given for the material prior to treatment with alkali. The three curves show similar features. The main endotherm occurred at about 1020 °C and is attributed to breakdown of CaCO_3 (45 p.s.i.). This peak was preceded at about 980 °C by a small endotherm believed to be the result of an inversion in the CaCO_3 (Mackenzie 1957; Winchell 1948). There was an endothermic peak at about 900 °C, which probably resulted from the final breakdown of illite (Gillott 1963a). The large peak at 780 °C corresponded to decomposition of the MgCO_3 part of the dolomite. This peak was small in the Kingston 0- to 24-ft sample and confirmed the result of X-ray analysis that the amount of dolomite was smaller than in either of the other two samples. There are exothermic peaks in the 300 to 500 °C range that resulted from the decomposition of organic material.

Thermograms of samples treated with alkali showed three new effects. An endothermic peak attributed to brucite appeared at about 440 °C; the endotherm at 780 °C showed a progressive reduction; and the 900 °C endotherm increased in the Kingston 0- to 24-ft and 6- to 7-ft samples.

The rapid growth of the brucite peak is clearest on the curves of the 0- to 24-ft samples (Fig. 7). The other Kingston sample and the mixture untreated with alkali gave thermograms that showed an exothermic peak at about 450 °C. This probably interfered with the endothermic peak brought on by brucite in the alkali-treated samples. A comparison of the brucite peak on the two series of curves, however, confirms the X-ray finding that dedolomitization was more rapid in the Kingston 6- to 7-ft samples than in the samples of the similarly constituted mixture.

The samples were analyzed under pressure in a CO_2 atmosphere to shift the CaCO_3 peak to a higher temperature (Mackenzie 1957). The progressive dedolomitization may be followed on the curves from the steady reduction of the MgCO_3 peak. Some caution is required in considering the magnitude of this peak as a measure of the quantity of dolomite remaining in the sample. Thermograms of samples that contained CaCO_3 , the acid-insoluble fraction of Kingston 6- to 7-ft, and Na_2CO_3 , but no MgCO_3 , displayed an endothermic peak at about 800 °C when analyzed at 45 p.s.i. in dynamic CO_2 . Although the

FIG. 7. Thermograms of Kingston rock. Sample composite of 24-ft section. Soaked in 2 M NaOH for increasing intervals of time. D.T.A. apparatus: R. L. Stone and Co.; settings: 50 μ V; 45 p.s.i.; dynamic gas, CO₂; 10°/min.

FIG. 8. Thermograms of Kingston rock. Sample from bed at 6- to 7-ft level in quarry. Soaked in 2 M NaOH for increasing intervals of time. D.T.A. apparatus: R. L. Stone and Co.; settings: 50 μ V; 45 p.s.i.; dynamic gas, CO₂; 10°/min.

samples used in the kinetic studies were washed there is a possibility that some Na_2CO_3 may have been retained. Also at about 450°C the $\text{Mg}(\text{OH})_2$ dehydroxylates, forming MgO . This may react (Mackenzie 1957) with the CO_2 used in the analysis, forming MgCO_3 . As there is no clear indication on the thermograms for carbonation of the MgO the effect was probably small. Furthermore, according to Webb and Heystek (Mackenzie 1957), MgCO_3 decomposes at a somewhat lower temperature than the MgCO_3 portion of the dolomite.

Kingston samples analyzed after increasing time intervals in alkali gave thermograms in which the endotherm at 900°C , attributed to illite, became progressively enhanced (Figs. 7, 8). There is no comparable increase of the corresponding peak on the series of curves obtained by analysis of the alkali-treated mixture (Fig. 9).

Results of Chemical Analysis

With increase in reaction time there was a steady fall in the concentration of NaOH in the solution and a corresponding increase in the concentration of Na_2CO_3 (Table II). The percentage concentration of Na_2CO_3 in the Kingston 6- to 7-ft powder showed an asymptotic increase with time in alkali; the concentration of Na_2CO_3 in the powdered mixture increased up to the seventh day and then showed a small decrease.

The dedolomitization reaction is most simply expressed by the following chemical equation:

The total concentration of Na_2CO_3 formed at a given time was determined so that it was possible to calculate the percentage of dolomite destroyed. As the initial dolomite content and the percentage of acid-insoluble material was known, it was also possible to calculate the percentage of dolomite remaining in the carbonate fraction. This value was compared with that obtained by X-ray diffraction. Fairly good agreement was found between the chemically derived result and that based on quantitative diffractometry for the powdered mixture and the Kingston 6- to 7-ft samples analyzed after 14 and 16 days in alkali. There was a discrepancy of 10% or more, however, for the Kingston 6- to 7-ft sample analyzed after 2 and 7 days in alkali (Table I). This discrepancy persisted when the analysis was repeated.

If NaOH reacts with some of the CaCO_3 as well as with the MgCO_3 in dolomite, $\text{Ca}(\text{OH})_2$ should appear as a product and the calcite peak on the diffractogram should fail to enhance. A slower rate of dedolomitization would be deduced from the X-ray results. For each molecule of dolomite destroyed in this way, the quantity of Na_2CO_3 formed would be twice that formed when only the MgCO_3 portion of the molecule is attacked. Hence the rate of dedolomitization deduced from the chemical results would appear faster than the rate deduced from the X-ray results. It is not possible therefore to account in this way for the discrepancy between the chemical and X-ray results.

FIG. 9. Thermograms of mixture. 50:50 Florida dolomite; Georgia white marble plus 10% acid-insoluble Kingston 6- to 7-ft bed. Soaked in 2 *M* NaOH for increasing intervals of time. D.T.A. apparatus: R. L. Stone and Co.; settings: 50 μ V; 45 p.s.i.; dynamic gas, CO₂; 10°/min.

TABLE II
Chemical analysis of alkali used in dilatometers

Time in NaOH	Initial		2 days		7 days		14 days		16 days	
	NaOH	Na ₂ CO ₃	NaOH	Na ₂ CO ₃	NaOH	Na ₂ CO ₃	NaOH	Na ₂ CO ₃	NaOH	Na ₂ CO ₃
Normality of soln. g/liter in soln. % Na ₂ CO ₃ in solid	1.8824 75.296 —	0.0252 1.3356 —	1.7416 69.664 —	0.0828 4.3884 1.492	1.4086 56.344 —	0.2938 15.5714 3.677	0.9930 39.720 —	0.6938 36.7714 3.285	0.9056 36.224 —	0.8492 45.0076 3.079
Normality of soln. g/liter in soln. % Na ₂ CO ₃ in solid	1.9980 1.8640 79.920 74.560 —	— 0.0320 — 3.392 —	— 1.6744 — 66.976 —	— 0.1338 — 7.0914 1.342	Kingston 6- to 7-ft 1.3598 — 54.392 —	0.3900 — 20.670 3.895	0.9848 — 39.397 —	0.8098 — 42.9194 4.721	0.9998 — 39.992 —	0.8394 — 44.4882 4.928

Results of Pore-Volume Distribution

All the samples studied had a very small pore volume, less than 0.05 ml per g. Results of pore-volume distribution were of only qualitative significance; at high pressures a very small pore volume was penetrated by the mercury. It was concluded that a significant proportion of the measured mercury movement resulted from compression of the sample, the sample holder, and the mercury. It was difficult quantitatively to subtract mercury movement due to these separate effects from mercury movement resulting from pore penetration at each successive increase of pressure. The method of mercury penetration is therefore considered unsuitable for the determination of the pore-size distribution of materials of very low total pore volume such as these rocks.

DISCUSSION OF RESULTS

Dolomitic samples sufficiently fine to undergo significant dedolomitization invariably registered expansion in the dilatometer. The volume increase probably occurred in the alkaline solution as such samples showed no increase in solid volume when tested in the cell.

Kingston 6- to 7-ft material and the corresponding artificial mixture were tested in the modified cell, which incorporated a capillary tube attached to the reservoir. The decrease in the volume of solution in the reservoir when the Kingston material was tested indicated a movement of solution from the reservoir into the compression chamber. This did not take place when the mixture was tested; instead, a volume increase was registered in the capillary connected to the reservoir. There is evidence that the movement of solution into the compression chamber in the Kingston material resulted from the uptake of water by the sample. This was indicated by studies of sorption isotherms (Feldman and Sereda 1961) and by early work on concrete, which showed that deterioration occurred where moisture was available (Swenson and Legget 1960; Swenson 1957). This uptake of water also explains why Kingston samples produced a greater volume increase in the cell than in the dilatometer.

The expansion registered in the dilatometer implies a decrease in the density of the system. The density of water near the surface of a solid may be different from that in bulk liquid. The problem has been considered in relation to clay minerals by Deeds and Van Olphen (1961) and by Low (1961). According to Low, water taken up by clays becomes more ordered and has a more open type of packing than in the liquid, so that such water occupies a larger volume.

The moisture movement that accompanies dedolomitization of the Kingston samples occurs whether the sample is in the dilatometer or in the cell. In the dilatometer a decrease in density in the uptaken water should register as a volume increase. As no water uptake is indicated for the mixture and as its dilatometric curve is closely similar to that produced by the Kingston material it would appear that any density change in the water taken up must be small. At any rate the resulting volume change accounts for only a small fraction of the total expansion.

Reaction between alkali and dolomitic mixtures and alkali and nonreactive

dolomitic rock causes an increase in the volume of the solution, but is not accompanied by imbibition of water. Reaction between alkali and Kingston rock leads both to an increase in the volume of the solution and to a movement of water into the solid. The water uptake causes an increase in the volume of the solid, and aggregate that behaves in this way causes distress and failure of concrete.

Evidently the ability to expand by moisture uptake is dependent upon factors other than those of composition, crystallite size, and strength of alkali. These additional factors almost certainly result from textural differences between reactive and nonreactive materials.

Kinetic studies of ball-milled reactive rock in both cell and dilatometer revealed a close correspondence between the rate of dedolomitization and the rate of expansion. The two are evidently closely related. It is highly probable that the dedolomitization reaction is closely connected with the moisture movement into the Kingston samples. This implies either the development or the presence within the solid of material with an affinity for water.

It has been suggested by Feldman and Sereda (1961) that the behavior would be satisfactorily accounted for by development of material with gel-like properties. Such properties are characteristic of materials within the colloidal size range. CaCO_3 and $\text{Mg}(\text{OH})_2$ are the only known solid products. Rapid crystallization or formation within restricted or confined spaces may lead to formation of very fine crystallites. The Kingston material has a very fine pore structure and undergoes more rapid dedolomitization than the mixture of similar composition. One may postulate that the $\text{Mg}(\text{OH})_2$ or CaCO_3 that formed was trapped within the pores as very fine crystallites of colloidal dimensions with gel-like properties. X-Ray powder-line profiles, however, showed little broadening. Calculations based on the half-peak breadths of the Fourier-unfolded pure diffraction profiles suggested that the mean crystallite size of the brucite was within the upper range of the colloidal state. The diffraction profiles of the $\text{Mg}(\text{OH})_2$ recorded from dedolomitized reactive rock were not detectably different from those recorded from the mixtures. The CaCO_3 peaks showed a steady growth as dedolomitization proceeded but the half-peak breadths were not greatly enhanced.

X-Ray evidence failed to confirm the hypothesis that gel-type reaction products form on dedolomitization of Kingston rock, but the presence within the alkali-treated solid of material of high surface area would account for many of the observed features of the reaction.

Coarsely powdered samples of Kingston 6- to 7-ft rock produced greater expansion in the cell than did samples reduced to the micron range by means of the ball mill (Fig. 3). This strongly suggests that greater textural damage resulted from finer grinding and impaired the ability of the rocks to expand. Microscopic examination shows that the coarsest component is dolomite. Hence these crystals are probably most severely damaged by ball-milling. In the Kingston rock the dolomite crystals contain inclusions, which are apparently of clay (Gillott 1963a). This clay will probably be set free in increased

quantities as progressively finer grinding breaks up more and more dolomite crystals. In the very finely ground rock the minerals approach the condition of a mechanical mixture. In such mixtures dedolomitization is not accompanied by an increase of solid volume. The reduced expansion in the cell displayed by very finely ground reactive rock shows that as its texture approaches that of a mechanical mixture the response to dedolomitization also becomes similar.

It is postulated that the essential difference between the mechanical mixture and the Kingston rock is that dedolomitization of the reactive material sets free clay minerals that were previously trapped, whereas there is no such result in the mixture. This released illite and chlorite is in an "active" state because the surface is unhydrated. Exchange sites on the enclosed clay minerals may be vacant or, more probably, occupied by Ca^{++} or Mg^{++} ions. On being released into the alkaline solution it is probable that some Na^+ ions will be adsorbed. A double layer will build up consisting of oriented water molecules with cations near the clay surface, balanced farther out by OH^- and CO_3^{--} ions. The development of the new double layer is accompanied by water uptake, which leads to the buildup of expansive forces that cause an increase of solid volume.

The expansive forces generated by hydration of illite and chlorite released by the dolomite may lead to the opening up of cracks and channels to clay held in the matrix. Alkali and moisture then gain access to this clay, which then also contributes to the expansion by the same mechanism as that of the clay minerals enclosed in the dolomite. The process may therefore eventually involve much of the illite and chlorite present in the rock.

On this hypothesis the dedolomitization reaction represents the first step in the expansive mechanism; it leads to expansion of the Kingston rock from exposure of the clay minerals. This accounts for the close relationship that exists between the rate of expansion and the rate of dedolomitization of the Kingston rock. Dedolomitization of the mixture is accompanied by no increase of solid volume because no new clay is released.

Additional support for the hypothesis comes from differential thermal analysis. Alkali-treated Kingston samples show an enhanced 900 °C endotherm. The effect is not shown by the mixture, suggesting that in the two types of samples the clay minerals responded differently to alkaline attack.

Adsorption studies showed that alkali-treated reactive rock had an increased surface area and a greater capacity for water retention (Feldman and Sereda 1961). Such a result accords well with the hypothesis now proposed. Clay minerals possess high surface area, and an increase in this property is to be expected from release of clay minerals previously enclosed and inaccessible to measurement. An increased capacity for water retention will also probably result from the newly formed double layer surrounding the clay particles.

The concentration of Na_2CO_3 determined by titration was used to calculate the percentage of dolomite remaining in the carbonate. All but one of the calculated values was higher than the value obtained by X-ray diffraction. This suggests that some Na_2CO_3 was not detected. It seems probable that some

CO_3^{--} ions were held within the double layer to balance the positive charge of the adsorbed cations near the clay surfaces. Washing may not have removed all the CO_3^{--} ions held in this way.

Studies with concrete beams showed that expansion was influenced by temperature. Beams held at 38 °C expanded more than similar ones held at 23 or 55 °C (Swenson and Gillott 1960). The increase in expansion at 38 °C may have resulted from an acceleration of the dedolomitization reaction. The decrease in expansion at 55 °C may be accounted for by the fact that increase in temperature is known to depress the hydrous double-layer surrounding clay (Lambe 1958a). The temperature increase from 23 to 55 °C probably accelerated the chemical reaction, but this effect was overshadowed when the temperature was further raised by the reduction in thickness of the double layer.

A quantitative test of the hypothesis would require a reliable estimate of the thickness of the hydrated double-layer and knowledge of the orientation taken up by the released clay particles. The double-layer is stated to be at a maximum in an alkaline environment (Lambe 1958b) but estimates of the thickness differ (Grim 1953). The orientation of clay crystallites may be parallel, random, or edge-to-face.

It is known that not all dolomitic rocks expand in alkali and it seems likely that texture as well as composition is significant. For a rock to be reactive it seems probable that crystal size must be fine enough for significant dedolomitization to occur, and that in addition the clay minerals must be so distributed that their surfaces become exposed as a result of the alkaline attack.

Powdered reactive rock from Kingston when treated with a dilute solution of long-chain fatty acids registered no expansion in the cell or dilatometer. This suggests that expansion of the aggregate in concrete may be prevented by the use of suitable surface-active agents. An investigation is in progress to determine whether this is so, and whether the use of treated aggregate has undesirable effects on other properties such as strength of concrete.

CONCLUSIONS

Conclusions may be summarized as follows:

1. Strong alkali reacts with dolomite to cause an overall increase in the volume of the system. In general there is no accompanying increase in solid volume and the expansion registered in the dilatometer probably occurs in the liquid phase.
2. Mixtures of the same composition as Kingston rock show no increase in solid volume when attacked by strong alkali.
3. The action of alkali upon reactive Kingston rock causes an increase of solid volume owing to water uptake.
4. Fine grinding causes textural damage to reactive rock that decreases its capacity for water uptake when attacked by strong alkali.
5. Textural damage is caused by release and exposure of clay minerals formerly enclosed within dolomite crystals.

6. The dedolomitization reaction is closely related to, but is probably not the direct cause of, expansion of the reactive rock.
7. Thermograms of alkali-treated Kingston rocks display an enhanced 900 °C endotherm. This implies participation in the reaction by the clay minerals that is not shown by compositionally similar mixtures.
8. When destruction of dolomite by strong alkali (dedolomitization) results in release of clay the latter has an unwetted surface and therefore is in an "active" state; it is quite different from the acid-separated clay in a mechanical mixture.
9. An equilibrium is established in which Na^+ , Ca^{++} , and Mg^{++} ions are adsorbed onto exchange sites on the newly exposed clay mineral surfaces, and a double layer develops.
10. Cracks open and allow water and alkali to gain access to clay minerals enclosed in the matrix. This clay responds similarly to that released from dolomite.
11. Expansion on dedolomitization of Kingston rocks results from water uptake by the newly exposed clay minerals owing to formation of the hydrous double layer.

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