Studies on the Mechanisms of Alkali-Carbonate Reaction

Part I. Chemical Reactions

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•AN understanding of the mechanisms of alkali-carbonate rock reaction which result in expansion of concrete is of primary importance in dealing with the resultant problems on a practical level. This paper reports results of laboratory studies made to determine the contributory chemical reactions that may take place. Results of parallel studies on such physical aspects as internal structure of and access of alkalies into various carbonate rock types are not included, but will be published at a later date.

The method of approach has been to consider each of the three major minerals or groups of minerals that normally make up carbonate rocks; i.e., quartz, clays and carbonates. These were investigated through studies of pure minerals, as well as reactive and non-reactive rocks, to determine what possible role each might play in observed expansion in the composite system.

These major constituents were analyzed and measured by a variety of methods to determine chemical composition, phase composition, and volume and mass of the materials before and after exposure to sodium and potassium hydroxide solutions. (Mass and weight are used interchangeably throughout this paper.) Evidences of reactions noted during this portion of the study were then sought in thin sections, test prisms, and in aggregate from laboratory and field concrete.

MINERALS AND ROCKS UTILIZED

The calcite and dolomite minerals used in this study were high-purity coarsely crystalline materials. The dolomite was the snow-white variety obtained from Wards Natural Science Establishment, Inc., and was shown by chemical analysis to contain 46.4 percent $MgCO_3$. The calcite was a clear-to-white vein material containing less than 1 percent $MgCO_3$ and was collected at Harrisonburg, Virginia.

Approximately 300 hand samples and data on their composition and expansivity as measured by the prism test described by Hadley (6) were available for this study from a previously conducted statewide survey for reactive carbonate aggregates from Virginia commercial aggregate sources (Newlon and Sherwood, 10). These rocks included a great variety of lithologic types exhibiting wide ranges in composition, texture and reactivity. Samples exhibiting extremes in composition and expansion as well as more representative rock materials were utilized from this suite.

EFFECT OF ALKALIES ON QUARTZ AND CLAY

Quartz

In all the rocks studied, quartz was present in quantities easily detected by thin section or X-ray analysis. The actual percent of quartz varied from about 1 to as high as 40. Petrographic studies indicated this material to be dominantly a dense, well-

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TABLE 1

ROCKS SELECTED FOR QUARTZ AND CLAY MINERAL STUDIES

Rock[1]	Ratio: Dolomite/Total Carbonate	Quartz (%)	Clay (%)	Prism Expansion, % (8 weeks)
1-8	0.63	9.5	16.3	0.69
5-1	0.18	6.5	13.1	0.13
26-5	1.00	1.0	4.8	0.02
35-6	0.09	8.0	1.0	0.01
22-2	0.80	2.0	18.5	-0.01
32-2	0.56	1.0	18.5	-0.02
1-17	0.03	2.0	1.0	-0.08

[1] The two-number designation of the rock samples has been carried over from the previous work (9). The first number designates the quarry, the second the sample taken from that quarry.

crystallized, clear quartz with only minor amounts of chert. However, a considerable amount of clay-sized quartz with a high surface area to volume ratio was present in all the samples and the susceptibility of this material to attack by strong alkalies might be suspected. To investigate this possibility, two chips for thin sectioning and 3 gm of -200 mesh material were prepared from each of several rocks showing a large variation in composition and reactivity (Table 1). One chip was soaked in 1N NaOH for three months, and one-half of the powdered rock was soaked for four weeks. (The effects of NaOH have received most attention in these studies because induced expansions of reactive rocks were previously determined to be greater with NaOH than with KOH (6, 9).) Subsequent to the alkali exposure, thin sections were made from both the soaked and unsoaked chips, and the rock powders were analyzed by X-ray diffraction. In each case, no significant change could be discerned in the amount or nature of the quartz present. The clay-sized fractions of the insoluble residue of these rocks were also exposed to strong alkali solutions and X-rayed for quartz with similar results.

These test results, together with lack of visible evidence (gel, etc.) of alkali-silica reaction in laboratory and field concrete, have led the authors to disregard quartz as a deleterious constituent in any of the carbonate rocks studied to date.

Clays

Clay minerals, like quartz, were present in every carbonate rock analyzed during this study. The amount of clay is often difficult to measure accurately because of problems encountered in separating the fine quartz particles from the clay fraction. Several X-ray methods have been suggested (1, 5), and the authors are now experimenting with modifications of these. Generally, X-ray diffraction methods using an internal standard for determining quartz in the insoluble residue of a carbonate rock and designating the remainder of the residue as clay, providing no other minerals are present in large amounts, have been found to be satisfactory for most of the work done to date. These techniques indicate that clay contents of more than 15 percent are not unusual in the Virginia carbonates.

To investigate the effects of strong alkali on the clay fraction of the carbonate rocks the seven samples given in Table 1, which represent both reactive and non-reactive rocks and also wide variations in the carbonate minerals and insoluble residue contents, were utilized. Each rock was ground to -50 mesh and treated with a 0.23N HCl, which was added in small increments until vigorous reaction ceased. This concentration was previously determined to have essentially no effect on the clay minerals present.

The clay fraction was separated, dried and identified by X-ray diffraction. The clay species found in both reactive and non-reactive rock from the Virginia portion of the Appalachian geosyncline are very similar, consisting almost entirely of a 10Å illite and a 14Å chlorite. This chlorite varies slightly from sample to sample but appears to be a magnesian variety.

Clay fractions of rocks 1-8, 5-1 and 1-17 which showed high, moderate, and no alkali reactivity, respectively, were each split into three parts. One-third was put into 1N NaOH and another in 1N KOH for a period of one year. The remaining one-third was kept sealed and dry as a standard. At the end of one year, all three parts were oriented by settling on glass slides and studied by X-ray diffraction. The only alteration evident in the X-ray diffraction patterns of the soaked versus unsoaked material involved the peaks representing d-spacings at approximately 7.68Å and 7.13A. The 7.68Å spacing seemed to have weakened during soaking, whereas the 7.13Å spacing appeared to have been reinforced. This phenomenon occurred with both NaOH and KOH exposures and was clearly evident in the clays from each rock type.

This alteration may be due to poorly crystallized chlorite (002 plane) being transformed to a better crystallized material during the soaking period. Heat treatment is reported to have this effect on some chlorites (3). The values of 7.1Å for this d-spacing is that generally evident in well-crystallized chlorites. In any case this minor alteration in crystal structure was observed to take place in both reactive and non-reactive rock and is of academic rather than practical significance in the present work.

EFFECTS OF ALKALIES ON POWDERED CARBONATE MINERALS AND ROCKS

Volume and Mass Changes

Based on the work of Swenson and Gillott (12), Hadley (6), and others, the breakdown of dolomite had been suspected as the major cause of the expansive alkali-carbonate reaction prior to the present work. The remainder of this paper is devoted primarily to data and observations taken from experiments investigating the effects of sodium and potassium hydroxides on calcite and dolomite mixtures and on carbonate rocks.

Mineral Calcite and Dolomite.—Experiments were designed to measure possible volume and mass changes in finely ground dolomite and calcite minerals exposed to alkali solutions. The first of these involved five discrete mixtures ranging from pure dolomite to pure calcite computed on a mole rather than a weight basis. Each of these mixtures was exposed to NaOH solutions with the following hydroxide to carbonate ratios:

$$\frac{\text{Equivalents of OH}^-}{\text{Equivalents of CO}_3^=} = 0,\ 0.25,\ 0.50,\ 0.75,\ \text{and}\ 1.00^1$$

All the mixtures were stored at 25 C in graduated cylinders and were stirred periodically for 22 weeks. At the end of this period the solid material was allowed to settle for several days to a constant level and its apparent volume was measured. Figure 1 shows the level of the solid materials after exposure to distilled water and to concentrated NaOH for 22 weeks.

Figure 2 shows the curves obtained by plotting apparent volume increase of solid material in the cylinders versus concentration of NaOH for several mixtures of calcite

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[1] Yielding NaOH concentrations of approximately 0, 1N, 2N, 3N and 4N, respectively, since the moles of carbonate and the volume of solution were kept constant. This rather unorthodox notation has been utilized in the present work because a primary concern was to determine how far these reactions would proceed toward completion in systems where not only concentration of solution but also the ratios of hydroxide to carbonate were known.

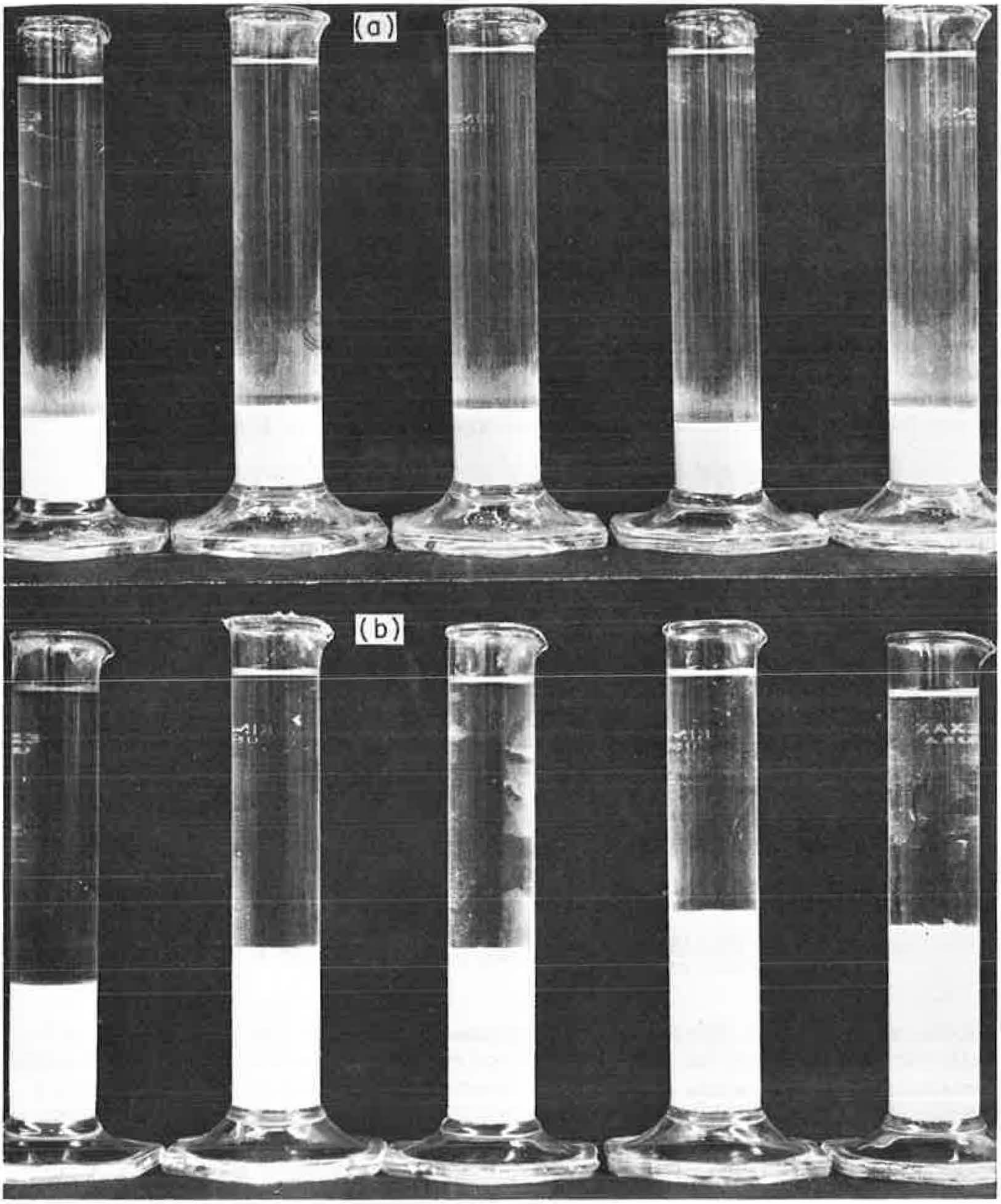

Figure 1. Mineral powders soaked for 28 weeks. Cylinders from left to right contain dolomite/total carbonate ratios of 0.00, 0.25, 0.50, 0.75, and 1.00: (a) effect of distilled water, and (b) effect of concentrated (Eq. OH^-/Eq. $CO_3^=$ = 1.00) NaOH solution.

and dolomite after twenty-two weeks. The data plotted in Figure 2 clearly show that: (a) mixtures ranging from all calcite to all dolomite exhibited significant apparent volume increases if the Eq. OH^-/Eq. $CO_3^=$ ratio was 0.50 or greater, and (b) volume change increased with increased dolomite content if NaOH was in the system. Parallel experiments showed no volume increase with time where dolomite powders were stored in distilled water.

The apparent volume increase of pure calcite is felt to be of particular interest, and the reactions which are thought to cause this are discussed in a subsequent section.

The second experiment was performed with KOH being used instead of NaOH. Again an apparent volume increase was observed. However two differences between the KOH and the NaOH soaks were noted. First, the observed increase in volume was nearly equal for a given concentration of KOH regardless of what mixture of calcite and dolomite was involved. Second, equilibrium in the system was very difficult to attain and probably was not reached in these mixtures. The experiments involving KOH were carried out several times over a period of months with stable temperature and frequent agitation, but the observed was about 25 percent for Eq. OH^-/Eq. $CO_3^=$ ratio of 1.0, and 15 percent for Eq. OH^-/Eq. $CO_3^=$ ratio of 0.5.

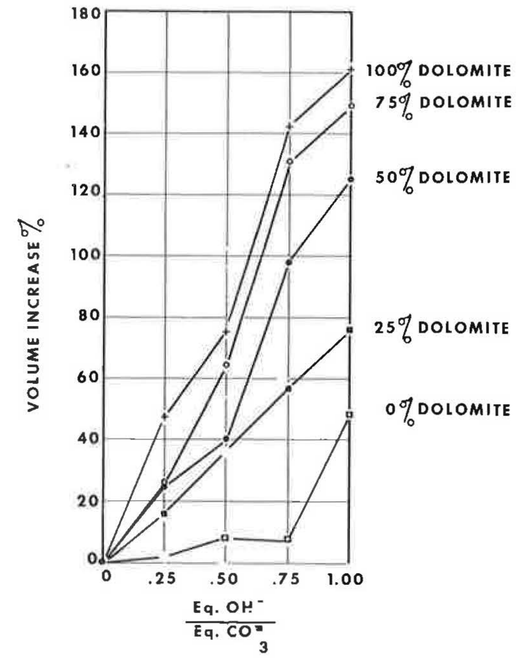

Figure 2. Volume increase vs concentration of NaOH at 22 weeks.

After volume measurements were completed for both the NaOH and KOH experiments, the mixtures were filtered, dried at normal temperature in a desiccator, and weighed. In general, the weight increases measured for the solid phases were similar to the apparent increases in volume. Table 2 gives the weight change measurements for 1.00 and 0.50 alkali to carbonate ratios of both the NaOH and KOH mixtures. Equilibrium conditions were probably not attained in every case, particularly in the KOH mixtures.

Rocks.—To substantiate the trends noted in NaOH soaks of the pure calcite and dolomite minerals, similar studies were made of carbonate rocks of widely different characteristics. Rock 1-8 is a highly expansive material with a relatively high insoluble residue content of 26 percent and near equal amounts of calcite and dolomite in the carbonate fraction. Rock 37-6 contracts slightly on prolonged exposure to NaOH. It contains a very low insoluble residue content of 1 percent and the carbonate is essentially all dolomite.

Five samples each of rocks 1-8 and 37-6, all containing equal moles of carbonate ion, were crushed to pass a number 200 standard sieve. Each sample was transferred to a graduated cylinder so that five cylinders were prepared for each rock, and equal amounts of carbonate ion were in all ten cylinders. NaOH solution was added to each rock, as in the mineral series, in increments of Eq. OH^-/Eq. $CO_3^=$ = 0.00, 0.25, 0.50, 0.75, and 1.00. The variation in the levels of the solid material at eight weeks is shown in Figure 3 for both rock types. Volume change versus time is shown in Figure 4.

Two points of possible significance are brought out by Figure 4: First, in rock powders with high surface area to mass ratios, volume increase is related directly to dolomite content regardless of the expansive tendencies exhibited by the original rock; and second, eventually expansion ceases with time and the curve levels off. The time required for completion of the expansive reaction is, of course, a function of grain

TABLE 2

WEIGHT CHANGE MEASUREMENTS OF FILTERED AND DRIED SOLIDS FROM REACTED ALKALI-CARBONATE MIXTURES

NaOH			KOH			Distilled Water		
Mole Ratio: Dolomite/Total Carbonate	$\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}$	Δ Weight Increase (%)	Mole Ratio: Dolomite/Total Carbonate	$\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}$	Δ Weight Increase (%)	Mole Ratio: Dolomite/Total Carbonate	Hydroxide	Δ Weight Increase (%)
0.00	1.00	40.2	0.00	1.00	31.6	0.00	0.00	-2.2
0.25	1.00	73.0	0.25	1.00	43.2	0.25	0.00	-1.7
0.50	1.00	94.8	0.50	1.00	31.4	0.50	0.00	-1.5
0.75	1.00	106.0	0.75	1.00	28.9	0.75	0.00	-1.9
1.00	1.00	120.0	1.00	1.00	29.9	1.00	0.00	-2.7
0.00	0.50	13.0	0.00	0.50	17.4			
0.25	0.50	28.8	0.25	0.50	19.6			
0.50	0.50	22.1	0.50	0.50	16.6			
0.75	0.50	26.7	0.75	0.50	20.4			
1.00	0.50	30.5	1.00	0.50	17.6			

size and agitation and not necessarily that shown in Figure 4. The expansion of the two rock powders ceased at the same time regardless of the percentage of dolomite present.

Figure 5 presents the data on volume change versus hydroxide concentration for the same rocks (1-8 and 37-6) at eight weeks. Concentrations of NaOH in excess of 0.50 did not result in increased volume change of the powdered 1-8. This is a probable result of all the dolomite reacting with NaOH and essentially no further expansive reaction taking place.

Identification of Reaction Products

After 22 weeks of exposure, the solid materials in each of the mineral NaOH soaks were filtered and dried, and selected ones were identified and semi-quantitatively analyzed by X-ray diffraction. The major finding of this X-ray work was the presence of considerable amounts of the hitherto unreported hydrated carbonate $CaNa_2(CO_3)_2 \cdot 5H_2O$, which is identical to the mineral gaylussite (see Table 3).

Figure 6 shows the X-ray diffractograms made of the dolomite mineral soaked in NaOH solutions of various concentrations. The sudden appearance and dominance of the gaylussite phase at high NaOH concentrations is graphically evident.

Table 3 shows that the gaylussite phase forms in considerable amounts when dolomite is exposed to high concentrations of NaOH. The reaction is less energetic, but clearly evident, when calcite is exposed in a similar manner. Intermediate mineral mixtures, as would be expected, show a progressive increase of the gaylussite phase with increased dolomite.

An interesting phenomenon brought out in Table 3 is the absence of calcite in the solid phase after equal equivalents of NaOH and dolomite have reacted. Sizable amounts of calcite remain when equal mole ratios of calcite and NaOH (lower right corner, Table 3) are reacted. The data indicate that the $CaCO_3$

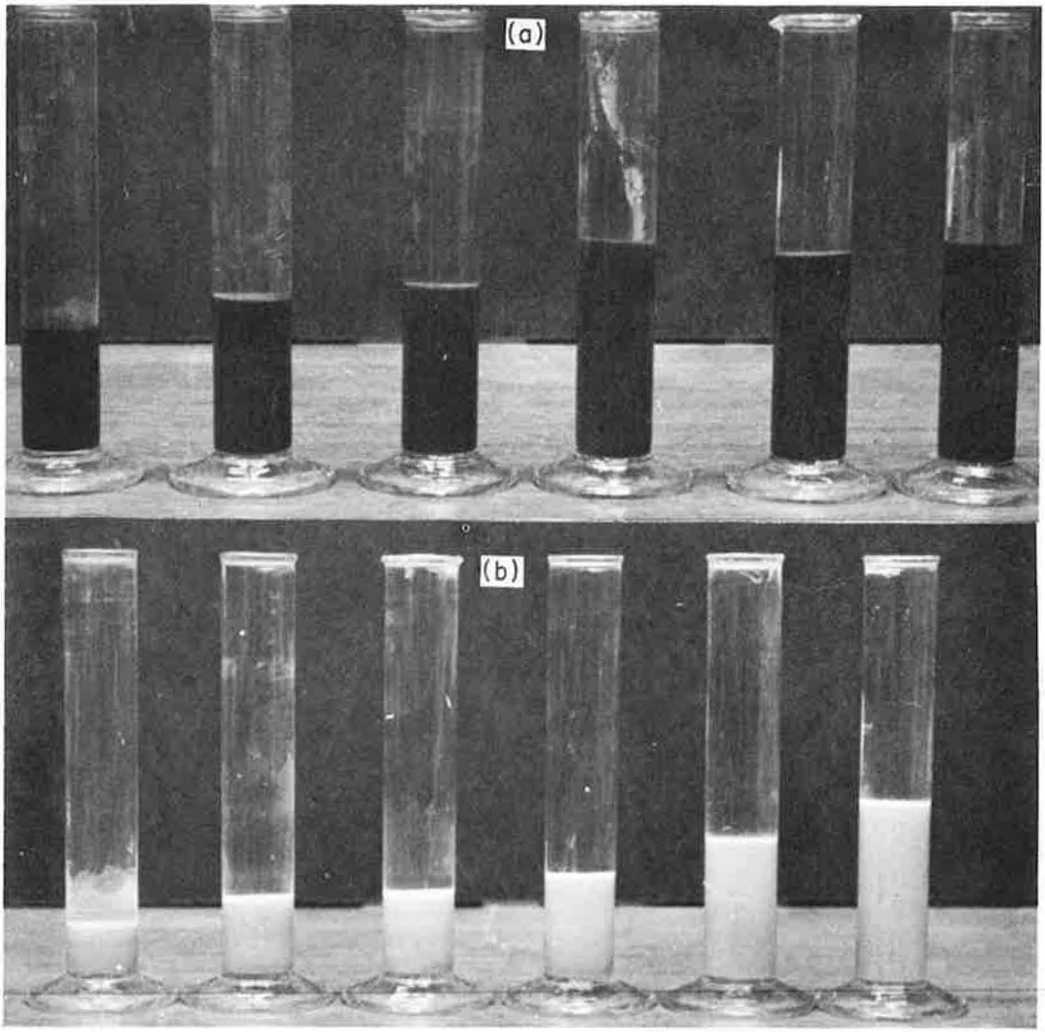

Figure 3. Rock powders soaked for 8 weeks. All cylinders contain equal moles of carbonate. Each set of cylinders contains NaOH solutions of the following concentrations (from left to right): Eq. of OH^-/Eq. of $Co_3^=$ = 0.00, 0.25, 0.50, 0.75 and 1.00: (a) contains aggregate 1-8, and (b) contains aggregate 37-6.

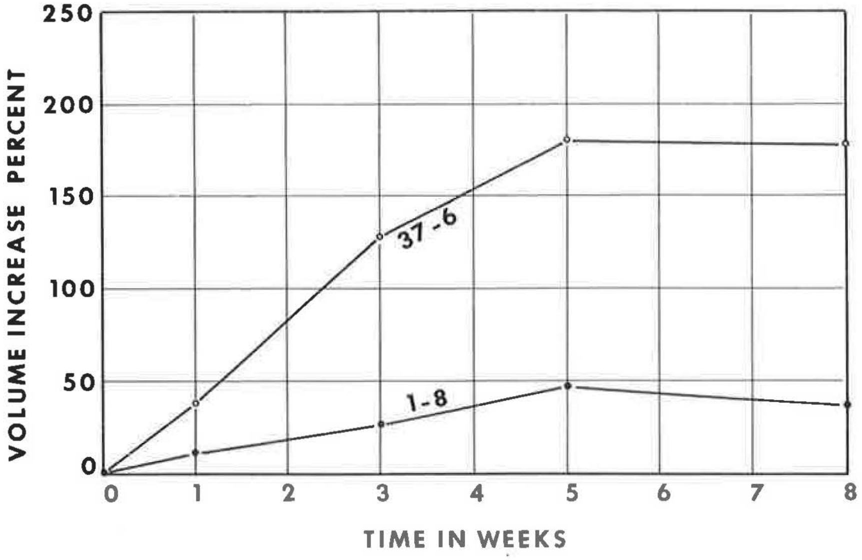

Figure 4. Volume change of powdered rock vs time. NaOH concentration Eq. OH^-/Eq. $CO_3^=$ equals one.

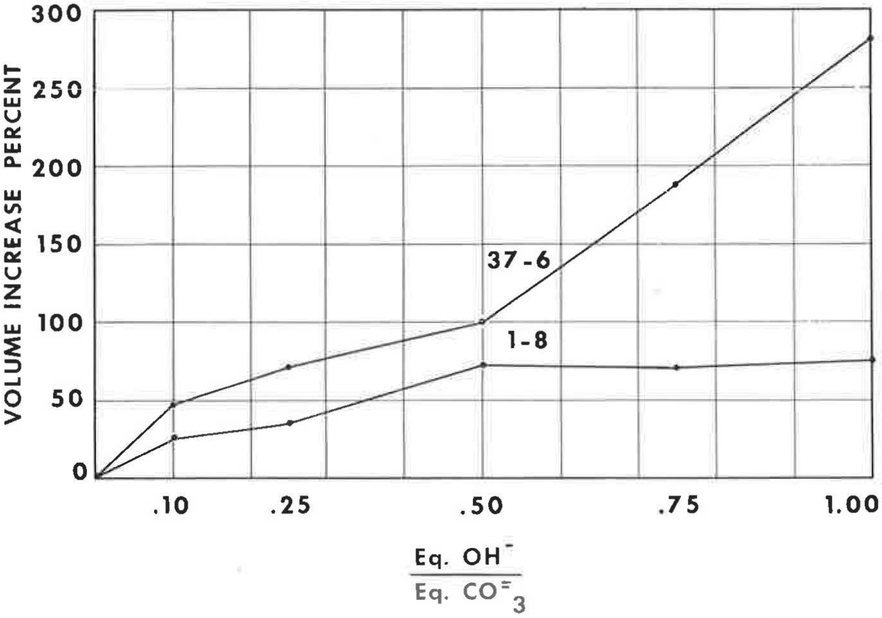

Figure 5. Volume change of powdered rock vs hydroxide to carbonate ratio at 8 weeks.

resulting from the breakdown of dolomite is considerable more reactive than the mineral calcite when exposed to NaOH solutions of equal normality.

Table 4 shows the phases present in KOH-carbonate mixtures. As in the case of NaOH the hydrated double salt, in this case, $Ca_2K_6(CO_3)_5 \cdot 6H_2O$, appears at high hydroxide concentrations. Other similarities to the NaOH reactants in Table 3 are (a) the

TABLE 3

PHASES PRESENT IN CARBONATE MINERAL—NaOH REACTANTS

Dolomite and Calcite (%)	NaOH $\left(\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}\right)$			
	0.25	0.50	0.75	1.00
Dolomite, 100	Calcite—moderate Dolomite—dominant Brucite—weak Gaylussite—not discernible	Calcite—moderate Dolomite—strong Brucite—weak Gaylussite—trace	Calcite—trace Dolomite—moderate Brucite—weak Gaylussite—dominant	Calcite—not discernible Dolomite—trace Brucite—moderate Gaylussite—dominant
Dolomite, 75 Calcite, 25	Calcite—strong Dolomite—strong Brucite—weak Gaylussite—not discernible	Not X-rayed	Not X-rayed	Calcite—weak Dolomite—trace Brucite—weak Gaylussite—strong
Dolomite, 50 Calcite, 50	Calcite—strong Dolomite—moderate Brucite—weak Gaylussite—not discernible	Calcite—dominant Dolomite—weak Brucite—weak Gaylussite—trace	Calcite—strong Dolomite—trace Brucite—weak Gaylussite—strong	Calcite—moderate Dolomite—trace Brucite—weak Gaylussite—strong
Dolomite, 25 Calcite, 75	Calcite—dominant Dolomite—trace Brucite—weak Gaylussite—not discernible	Not X-rayed	Not X-rayed	Calcite—strong Dolomite—trace Brucite—trace Gaylussite—strong
Calcite, 100	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—trace	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—trace	Calcite—dominant Dolomite—not discernible Brucite—not discernible Gaylussite—weak	Calcite—strong Dolomite—not discernible Brucite—not discernible Gaylussite—weak

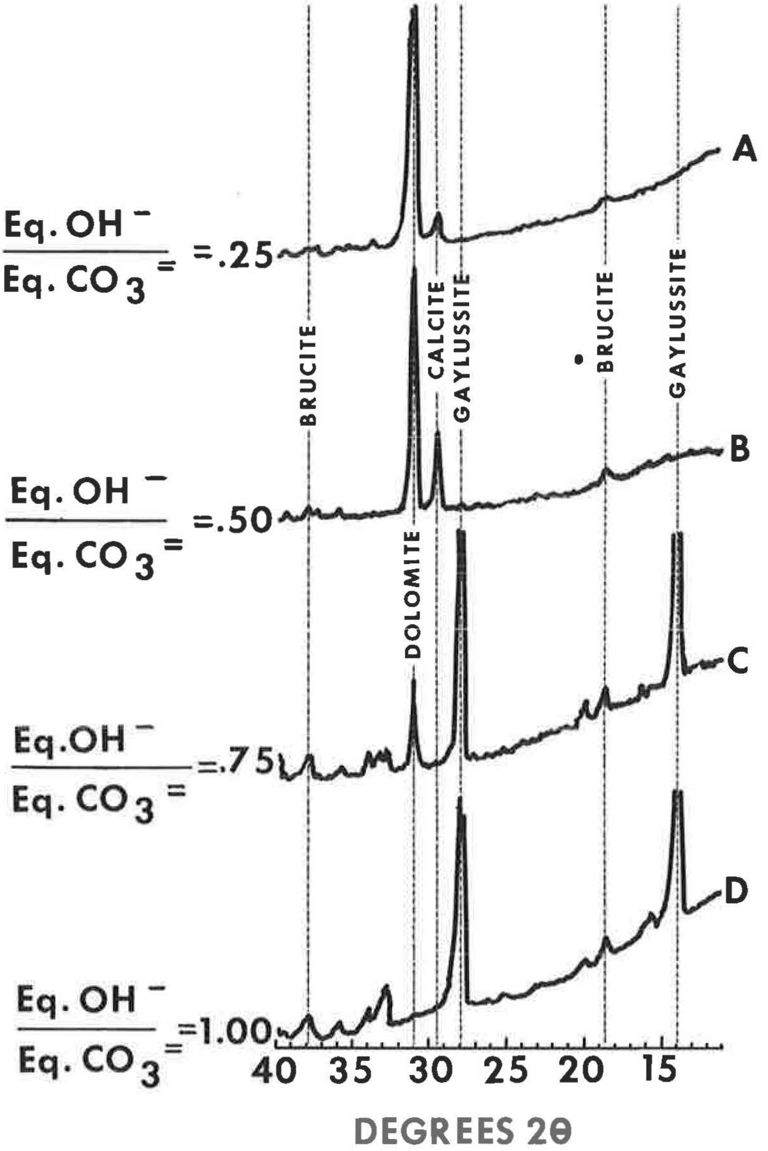

Figure 6. X-ray diffractometer tracings of mineral dolomite powders exposed to NaOH of different concentrations for 22 weeks. Diffractometer strips A, B, C and D were made from dolomite exposed to NaOH of Eq. OH^-/Eq. $CO_3^=$ = 0.25, 0.50, 0.75 and 1.00, respectively.

TABLE 4

PHASES PRESENT IN CARBONATE MINERAL-KOH REACTANTS

Dolomite and Calcite (%)	KOH $\left(\frac{\text{Eq. OH}^-}{\text{Eq. CO}_3^=}\right)$	
	0.50	1.00
Dolomite, 100	Calcite—strong Dolomite—very strong Brucite—moderate Portlandite—not discernible Buetschliite—not discernible	Calcite—not discernible Dolomite—very strong Brucite—moderate Portlandite—weak Buetschliite—strong
Dolomite, 75 Calcite, 25	Not X-rayed	Calcite—moderate Dolomite—strong Brucite—moderate Portlandite—moderate Buetschliite—moderate
Dolomite, 50 Calcite, 50	Calcite—strong Dolomite—strong Brucite—weak Portlandite—not discernible Buetschliite—not discernible	Calcite—moderate Dolomite—strong Brucite—moderate Portlandite—strong Buetschliite—strong
Dolomite, 25 Calcite, 75	Not X-rayed	Calcite—very strong Dolomite—moderate Brucite—trace Portlandite—strong Buetschliite—strong
Calcite, 100	Calcite—dominant Dolomite—not discernible Brucite—not discernible Portlandite—trace Buetschliite—not discernible	Calcite—very strong Dolomite—not discernible Brucite—not discernible Portlandite—strong Buetschliite—strong

formation of calcite accompanying the breakdown of pure dolomite at Eq. OH^-/Eq. $CO_3^=$ of 0.50 or lower, and (b) the formation of brucite wherever dolomite has been attacked. An additional phase produced by these reactions, but not evident in the equivalent NaOH reactions, is $Ca(OH)_2$, or portlandite. In concrete this $Ca(OH)_2$ together with the $Ca(OH)_2$ produced by hydrating cement might slow or even halt the reaction according to the law of mass action. The chemical equations which explain the reaction products given in Tables 2 and 4 are developed in the following section.

As noted earlier, it appears that equilibrium has not been attained in these mixtures. This is indicated by a variation in the previously discussed mass changes and in the amount of reaction products shown by duplicate KOH-mineral soaks. Also, it is noteworthy that very strong dolomite peaks are still evident after 20 weeks in mixtures containing equal equivalents of KOH and dolomite. As previously mentioned, this peak had completely disappeared in the NaOH soaks of equal concentration in less than 22 weeks.

Chemical Reactions

Following the identification and semi-quantitative analyses of the solid portions of the hydroxide-mineral soaks given in Tables 3 and 4, the filtrates were allowed to evaporate at room temperature. The precipitates thus obtained were identified by X-ray diffraction to be dominantly hydrous alkali carbonates and hydroxides. Inasmuch as both the compounds which went into these reacting systems and those present after reaction were then known, the following significant chemical equations in these systems could be developed

Reaction equations involving NaOH:

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Concentrated}}{2NaOH} + 5H_2O \rightarrow \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\text{Gaylussite}}{CaNa_2(CO_3)_2 \cdot 5H_2O} \tag{1}$$

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Dilute}}{2NaOH} \longrightarrow \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\text{Calcite}}{CaCO_3} + Na_2CO_3 \tag{2}$$

$$\underset{\text{Calcite}}{2CaCO_3} + \underset{\text{Concentrated}}{2NaOH} + 5H_2O \longrightarrow \underset{\text{Gaylussite}}{CaNa_2(CO_3)_2 \cdot 5H_2O} + Ca(OH)_2 \tag{3}$$

Reaction equations involving KOH:

$$\underset{\text{Dolomite}}{18CaMg(CO_3)_2} + \underset{\text{Concentrated}}{44KOH} + 42H_2O \rightarrow \underset{\text{Buetschliite}}{7Ca_2K_6(CO_3)_5 \cdot 6H_2O} + \underset{\text{Brucite}}{18Mg(OH)_2} + 4Ca(OH)_2 + K_2CO_3 \tag{4}$$

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} + \underset{\text{Dilute}}{2KOH} \longrightarrow \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\text{Calcite}}{CaCO_3} + K_2CO_3 \tag{5}$$

$$\underset{\text{Calcite}}{6CaCO_3} + \underset{\text{Concentrated}}{8KOH} + 6H_2O \longrightarrow 4Ca(OH)_2 + \underset{\text{Buetschliite}}{Ca_2K_6(CO_3)_5 \cdot 6H_2O} + K_2CO_3 \tag{6}$$

Notes:

(a) Eqs. 2 and 5 were originally proposed by Hadley (6).

(b) Eq. 4 was developed to explain the observed reaction products by combining the following two equations for the reactions which are thought to take place:

$$3CaMg(CO_3)_2 + 6KOH + 6H_2O \rightarrow Ca_2K_6(CO_3)_5 \cdot 6H_2O + 3Mg(OH)_2 + CaCO_3$$

$$8KOH + 6CaCO_3 \longrightarrow 4Ca(OH)_2 + Ca_2K_6(CO_3)_5 \cdot 6H_2O + K_2CO_3$$

(c) In accordance with Hadley's (6) theory, the $Ca(OH)_2$ evolving during cement hydration could react with the alkali carbonate (and the hydrated double salts) shown on the right side of these equations, in more or less degree, to produce more alkali in solution.

It should be noted that these equations are based on the formation of reaction products in system open to the atmosphere.

Stability Reactions

Unlike the system Ca, Mg, CO_3, H_2O, the stability relations which have received a great deal of attention from geochemists, the similar systems Na, Ca, CO_3, H_2O and K, Ca, CO_3, H_2O, which are of major interest in the alkali-carbonate reactions, are only slightly known.

Only these two systems are discussed in this work, because the extreme insolubility of $Mg(OH)_2$ would normally serve to remove magnesium ions from solution in concrete. In one of the earliest references found on reactions in the system Na, Ca, CO_3, H_2O, Pratolongo (11) reports that at normal temperatures a 5 percent solution of Na_2CO_3 will react with $CaCO_3$ to produce gaylussite as a stable phase only when Na_2CO_3 is in solution in amounts greater than 14 percent. Also they determined that the gaylussite-pirssonite

($CaNa_2(CO_3)_2 \cdot 2H_2O$) join is at approximately 38 C with the pirssonite phase above this temperature, which indicates that pirssonite would not form at ordinary environmental temperatures. However, Lea and Desch (7) report temperatures in excess of this figure during maximum hydration of some mass concrete. Berg and Borisova (2), working on the solubility isotherms in the system Ca, Na, CO_3, H_2O, give the relative solubilities of calcium and sodium bicarbonates and the composition of the appropriate solid phase in equilibrium at normal temperature. These solid phases are progressively $CaCO_3$, $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $NaHCO_3$ as $Ca(HCO_3)_2$ decreases and $NaHCO_3$ increases in solution.

The system K, Ca, CO_3, H_2O has received very little attention in the literature. Milton and Axelrod (8), in their work on fused wood-ash stones, verified the presence of phases $Ca_2K_6(CO_3)_5 \cdot 6H_2O$ and $CaK_2(CO_3)_2$ and named them buetschliite and fairchildite, respectively, after earlier workers in this system. They observed the slow alteration of fairchildite to buetschliite in the presence of moisture at normal temperature but give no further details on the stability relationships over a range of temperatures and concentrations.

In general it is felt that the reactions in the present work are in good agreement with information available in published works. That gaylussite and buetschliite should occur when the hydroxide solutions are concentrated and not occur when the hydroxide solutions are dilute, would be expected, if, as shown by Hadley (6) and substantiated in this work, dolomite is broken down and magnesium in the form of $Mg(OH)_2$ is removed from the system. This would result in the formation of the alkali carbonate which in turn would react with the $CaCO_3$, present as calcite or as a reaction product from the dolomite, in a manner consistent with that noted in the published data. However, that there may be difficulties in attaining equilibrium in these systems is indicated by discrepancies that exist between the findings of Pratolongo (11) and that of Bury and Redd (4) regarding the amount of Na_2CO_3 required to react with $CaCO_3$ to form gaylussite, and in the difficulties experienced in the present study in obtaining consistent data on mass and volume changes when dolomite and calcite were exposed to KOH solutions.

IDENTIFICATION OF REACTION PRODUCTS IN CARBONATE ROCKS EXPOSED TO ALKALI

The transition from the high surface area to mass ratios which characterizes the minerals and rocks in powdered form to the low surface area to mass ratios of aggregate particles radically alters the rates, and possibly the types, of reactions. To evaluate the data obtained in the studies of finely ground materials, a series of investigations were made on rock prisms and aggregates with much less surface exposed to the alkali environment.

The major difficulty involved in this portion of the study was in the identification of the very small amounts of the reaction products available. Chemical analyses and chemical beneficiation treatments cannot be used in determining the reaction products because of the similar chemistry of the carbonate minerals and the material being sought. Optical and X-ray diffraction studies appear to hold the most promise, if proper techniques can be developed. The major effort in this work has involved X-ray methods.

Laboratory Prisms

Based on the very clear results obtained with the finely divided mineral and rock powders, the following compounds were accepted as the major phases to be sought: sodium and potassium carbonates, brucite, gaylussite, and buetschliite. A number of rock prisms 1/4 by 1/4 by 1 1/4 in., which had been used in expansion studies and exposed to 1N NaOH for one year, was selected for study. The composition of the surface layers was identified by X-ray diffraction. Table 5 shows that brucite and gaylussite were clearly evident in the expansive prisms and not evident in the two non-expansive ones.

TABLE 5

X-RAY EVIDENCE OF BRUCITE AND GAYLUSSITE IN CARBONATE ROCK MATERIAL EXPOSED TO NaOH

Aggregate	8-Week Prism Expansion	Powder		Prism	
		Brucite	Gaylussite	Brucite	Gaylussite
12-9	1.04	Moderate	Moderate	Moderate	Trace
12-4	0.78	Moderate	Moderate	Moderate	None
1-8	0.69	Strong	Strong	Moderate	Trace
5-1	0.13	Moderate	Strong	Moderate	Moderate
39-4	0.00	Not run		None	None
13-6	-0.01	Not run		None	None

Field Concrete

In addition to the investigation of the laboratory-treated materials, considerable effort was expended toward finding reaction products in the aggregate from distressed field concrete. Two 4-in. cores were taken from each of two structures which were known to contain reactive rock and which had shown cracking and evidence of expansion. These cores, designated W-1 and C-2, were broken in the laboratory and several samples of the fresh rock were scraped from the areas adjacent to the aggregate-mortar interface. These materials were X-rayed several times utilizing maximum settings on both the log and linear scales. One sample yielded a small peak at $28°2\theta$ which is the major peak for gaylussite. Upon heating for three hours at 200 C, the peak, instead of disappearing, increased in size; this indicated that the material was not gaylussite and its identity is as yet undetermined. All of the other suspected reaction products were checked with negative results, except for brucite, which appeared to be present in trace amounts.

The second method attempted was that of heavy media separation of the lighter reaction products from the remainder of the aggregate using bromoform-benzene solutions with specific gravities of 2.50 and 2.60. The finely ground aggregate in these liquids was allowed to settle, then the upper levels of the solid material were removed and analyzed by X-ray diffraction. Again the results were either negative or, at best, inconclusive.

Inasmuch as these attempts to identify the suspected reaction products were unsuccessful, a completely different approach to the problem was made. Several grams of clean aggregate fragments were taken from concretes W-1 and C-2. This material was powdered and carefully sieved. A 3-gm sample of the minus 200 to plus 325 portion was weighed to the nearest 0.0001 gm. The same procedure was carried out for a piece of the same aggregate type (1-8) which had been taken directly from the quarry. Each of the 3-gm samples was then put into 100 ml of hot distilled water and agitated for 10 min. The suspension was filtered, dried and weighed. This whole procedure was performed three times with the results given in Table 6.

These differences, while not great, appear to be consistent and are interpreted to indicate the presence of small amounts of relatively soluble reaction products in the aggregate from the concrete. To check this, the filtrates of two of the soaks were allowed to evaporate and the third was analyzed for calcium, sodium, and potassium in solution; the results are given in Table 7.

Table 7 shows that significant amounts of the alkalies from the cement have migrated into the aggregate. Finally, the residue from the evaporated filtrates was identified by X-ray diffraction using the powder camera. The calcium carbonate pattern was strong in each film. However, samples C-2 and W-1 each contained d-values indicative of the bicarbonates or hydrous carbonates of potassium and sodium. It is interesting

TABLE 6

WEIGHT LOSS (Percent) IN HOT DISTILLED WATER

Sample	First Run	Second Run	Third Run	Average
Quarry rock (1-8)	1.18	1.11	1.38	1.22
Concrete aggregate (C-2)	1.23	1.32	1.50	1.35
Concrete aggregate (W-1)	1.40	2.11	1.48	1.66

TABLE 7

ANALYSES OF FILTRATES

Sample	PPM in 100 Ml Filtrate		
	Calcium	Sodium	Potassium
Quarry rock (1-8)	7.0	1	7.5
Concrete aggregate (C-2)	4.5	9.8	29.9
Concrete aggregate (W-1)	7.0	3.5	21.0

to note that in samples C-2 and W-1 calcium carbonate predominated in the X-ray diffractogram, despite the fact that according to Table 7 sodium and potassium salts were probably present in greater amounts. This observation may explain why the alkali reaction products in affected concrete aggregates are so difficult to identify.

Finally, because the concretes represented by samples C-2 and W-1 are now essentially dry in the field, it appears logical to assume that at some stage subsequent to placement of the concrete the alkali concentrations of solutions within the aggregates must have become quite high.

DISCUSSION AND CONCLUSIONS

A principal aim of this work has been to investigate the chemical reactions taking place in open, aqueous systems containing calcite, dolomite, and sodium or potassium hydroxide. The breakdown of dolomite and the resulting volume and mass changes which take place were observed throughout a range of hydroxide concentrations and carbonate types. However, the effect of this breakdown on the actual observed expansion of certain carbonate rocks must be viewed as only part of a complex interplay of variables.

Access of hydroxides and the intrinsic rock strength to resist volume changes, resulting from the nature and geometry of grain boundaries, are of primary importance in determining rock expansion. In addition, the environment of hydrating cement in concrete superimposes a complex chemistry over the alkali-aggregate reaction which may radically alter the reaction rate and the formation of certain phases. Until these other parameters have been investigated in detail, the relative effects of each variable considered in this work must remain as a matter of conjecture.

The data presented here, tempered in light of earlier work, are thought to justify the following conclusions:

1. Quartz and clay in the carbonate rocks quarried in Virginia are not appreciably affected in the expansive alkali reaction of the host rock.
2. Finely ground dolomite and calcite minerals and carbonate rocks increase in volume and mass when exposed to NaOH and KOH solutions.
3. The amount of apparent volume and mass increases is directly related to the dolomite content for any given concentration of NaOH, whereas increases in volume and mass for the various carbonate mixtures are nearly equal for a given concentration of KOH.

4. The volume and mass change is accompanied by the breakdown of the mineral dolomite where this mineral is present.

5. In the open systems (exposed to air) used in this study the breakdown of dolomite yields calcite and brucite in low concentrations of NaOH and KOH; i.e., when Eq. OH^-/ Eq. $CO_3^=$ = 0.50, and brucite and gaylussite or buetschliite in high concentrations; i.e., when Eq. OH^-/Eq. $CO_3^=$ = 0.75.

6. Brucite and gaylussite have been identified at prism surfaces of reactive rock soaked in NaOH in the laboratory.

7. Brucite has been tentatively identified in the aggregate from distressed field concrete.

8. Analyses of rock from distressed concrete and identical rock directly from the quarry showed significantly higher concentrations of Na and K in the aggregate from the concrete.

9. X-ray diffraction identification of residues obtained by, soaking filtering and evaporating the filtrate of powdered aggregate from distressed concrete indicates the residue to contain $CaCO_3$ and some mixture of bicarbonates and hydrous carbonates of sodium and potassium. As of this writing, however, the exact nature of the sodium and potassium bearing phases in the reacted aggregate is unknown.

10. The identification of high volume, low specific gravity phases, such as gaylussite $CaNa_2(CO_3)_2 \cdot 5H_2O$ and buetschliite $Ca_2K_6(CO_3)_5 \cdot 6H_2O$, and the indirect evidence that hydrated carbonates and bicarbonates of sodium and potassium may occur in alkali-carbonate systems appears to provide a rational mechanism for observed carbonate rock expansions.

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