A Survey for Reactive Carbonate Aggregates in Virginia

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•THE DISCOVERY of alkali-reactive carbonate rocks in a Virginia quarry producing aggregates otherwise acceptable under Virginia Department of Highways Specifications (8) immediately suggested the necessity of determining the occurrence of these materials in other producing quarries. In addition to the need to know the location of reactive aggregates, the possibility of correlating the expansive behavior of such rocks with stratigraphy or mineralogy was also of considerable interest.

This paper presents data obtained from tests on rock samples taken in a survey of active quarries furnishing carbonate aggregates for concrete used by the Virginia Department of Highways. The shaded portion of the map in Figure 1 delineates those areas of Virginia underlain by carbonate rocks. Quarries which produce stone used in the Virginia highway system and which were sampled for this study are marked by the solid dots. The areas underlain by limestone and dolomite and the quarries producing carbonate aggregates are concentrated in the Valley and Ridge Physiographic Province. Only two quarries producing carbonate material for concrete are outside this area; they are located in the Arch or Everona marble in the Piedmont portion of the state.

The primary objectives of the survey were to determine: (a) the frequency of occur-

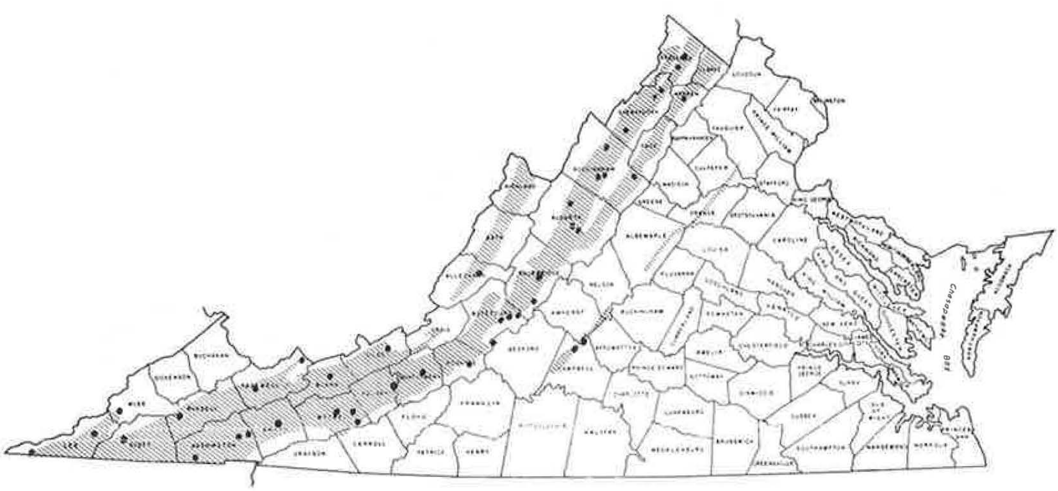

Figure 1. Location of quarries sampled. Shaded areas represent extent of carbonate rocks exposed in Virginia; solid dots show individual quarry locations.

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rence and volume of reactive carbonate aggregates being produced in Virginia, (b) the geographic and stratigraphic distribution of this material, (c) the lithologic characteristics of the expansive rocks, and (d) any correlations which might exist between mineralogic composition and expansive or other reactive behavior.

Investigations of the samples included measurement of susceptibility to alkali reaction by the prism test (5), formation of rims in mortars as discussed by Bisque and Lemish (1, 2, 3), determination of carbonate mineralogy and insoluble residue, and studies of thin sections.

The approach adopted in the survey was to gather limited samples from a large number of quarries. These preliminary samples would serve to satisfy the aforementioned objectives as well as to indicate the need for more extensive and detailed sampling of quarries containing reactive beds.

METHOD OF SAMPLING

Prior to sampling, a rapid survey of each of the quarries shown in Figure 1 was made to determine the different lithologies exposed in the workings. Oriented samples were collected from each lithologic type where quarry walls were accessible; where they were inaccessible, samples were taken from blast material. A total of 224 samples were collected from 42 quarries. The number of samples taken from any particular quarry varied from 2 to 15, depending on the size of the quarry and the degree of variation between the beds exposed.

Table 1 gives the geologic formations exposed in the quarries, together with the total number of samples taken from each formation and the number of quarries involved. This listing indicates that more of the carbonate aggregates used in the state are quarried from the Beekmantown than from any other formation, with the Elbrook, Shady (Tomstown) and Conococheague formations being nearly equal and next in importance as sources of supply.

TABLE 1

STRATIGRAPHIC DISTRIBUTION OF SAMPLES[1] TAKEN IN STATEWIDE SURVEY

Period	Formation or Member	No. of Samples	Quarries Involved
Mississippian	Newman Seam	7	1
Devonian	Licking Creek	5	1
Ordovician	Lowville (Moccasin)	10	2
	Ward Cove-Whitten (undifferentiated)	16	2
	Edinburg (Athens)	13	5
	Effna (Holston)	2	1
	Lincolnshire (Lenoir)	3	1
	Whistle Creek (Lenoir)	1	1
	New Market-Five Oaks (Mosheim)	10	6
	Beekmantown (Upper Black Beds)	13	3
	Beekmantown (other)	55	13
Cambrian	Conococheague	23	3
	Elbrook (plus Honaker)	29	4
	Rome (Waynesboro)	6	1
	Shady (Tomstown)	25	6
Pre-Cambrian (?)	Arch or Everona	6	2

[1]Contains only those formations sampled and is not meant to be a complete geologic column.

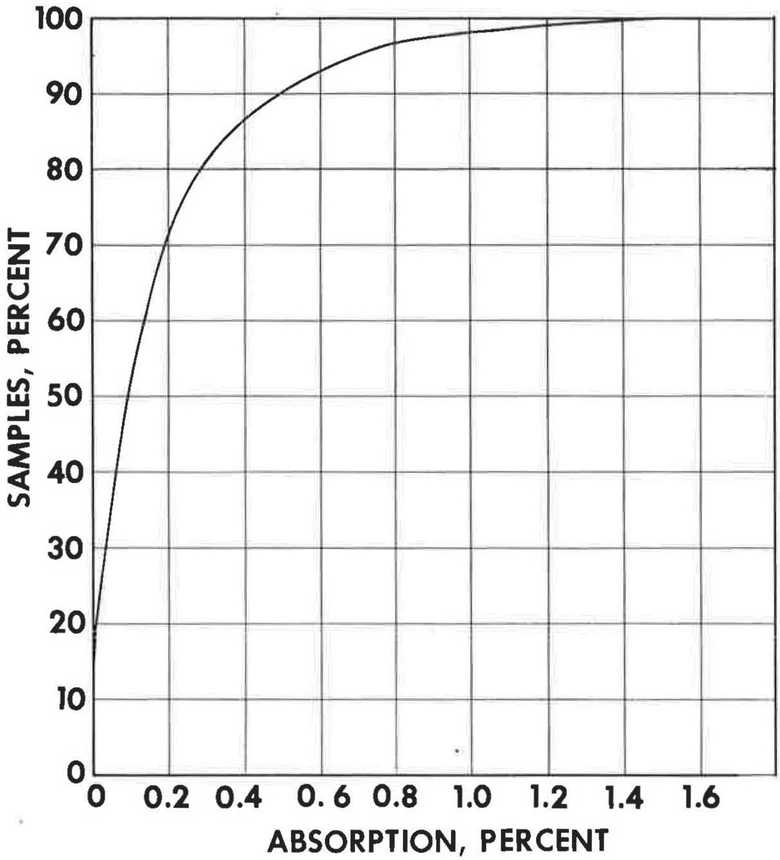

Figure 2. Cumulative curve showing percent of samples vs percent absorption.

ANALYSES OF SAMPLES

Physical Characteristics

Because of the large number of quarries involved and the preliminary nature of the survey, only small hand specimens weighing approximately 1,000 gm were collected. Thus, conventional measures of physical soundness could not be obtained. The vast majority of the rock samples, both expansive and nonexpansive, would, however, be considered physically acceptable. An appreciation of the general quality of the materials may be gained from the fact that each quarry produces concrete aggregate which, at the time of sampling, was required to meet the limits in Table 2.

The specific gravity and absorption after 24 hr of soaking were determined for each sample. The bulk specific gravities fell within the range 2. 65 to 2. 85. Approximately 98 percent of the samples had absorptions less than 1 percent (Fig. 2).

TABLE 2

SPECIFICATION REQUIREMENTS FOR GRADE A CONCRETE AGGREGATES USED IN VIRGINIA

Test	Max. Loss	
	Condition	(%)
Abrasion Resistance (AASHO T 62)	500 rev.	35
$MgSO_4$ Soundness (AASHO T 104)	5 cycles	8

Mineralogy of Samples

Carbonate Mineralogy. --The percentage of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) present in the carbonate fraction of each sample was determined by X-ray diffraction, following the method of Tennant and Berger (11). Samples of

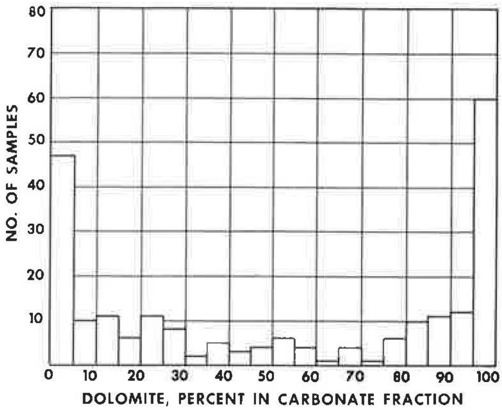

Figure 3. Distribution of carbonate compositions of test samples.

the ledge rock were prepared for X-ray analysis by hand grinding approximately 5 gm of sample to pass a No. 200 sieve. The powder was then transferred to a steel ball mill and tumbled for 17 hr. Most of the resulting powder passed a No. 325 sieve. This powder was packed into a standard well-type holder and the surface was made smooth with a glass plate. Nickel-filtered copper radiation with a 1^0 divergence slit and 0.003-in. receiving slit was used for the analyses. Scanning was done at a rate of 2^0 of 2θ per min for the 10^0 interval between 25^0 and 35^0 where the major peaks for calcite and dolomite appear. Areas under the peaks were measured with a planimeter and the ratios for the dolomite/calcite peaks were compared to a standard curve constructed previously to determine the percentages of each mineral in the carbonate fraction. This procedure, if properly and carefully performed, has been shown by Diebold, Lemish and Hiltrop (4) to be accurate to within 1 mole percent.

The distribution of carbonate compositions (Fig. 3) indicates that relatively pure limestones and dolomites are more prevalent in this group of samples than are mixtures of the two in nearly equal proportions. This carbonate distribution is similar to that noted previously in the literature for a suite of carbonate rocks of similar age in Illinois (6). The apparent scarcity of the intermediate compositions is not well understood at the present time.

Insoluble Residues.--The noncarbonate portion of the Virginia limestones and dolomites is generally composed of acid-insoluble silicates, such as quartz and clays. The

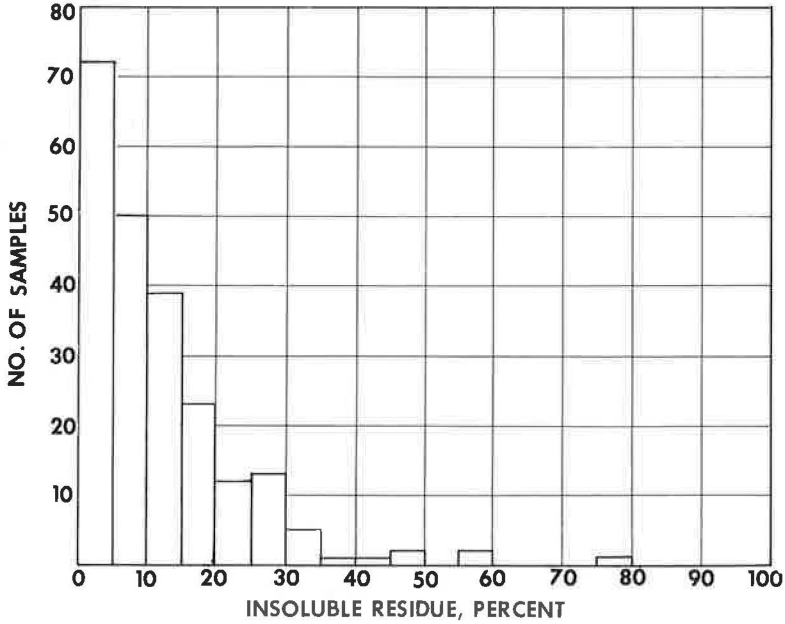

Figure 4. Distribution of insoluble residues determined for test samples.

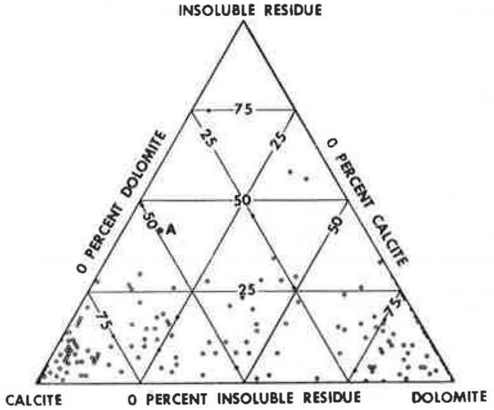

Figure 5. Ternary plot of composition of test samples.

percentages of insoluble residue were obtained by weighing a pulverized sample of the rock and treating it with an excess of concentrated HCl. When reaction was complete the residue was washed, dried, and weighed. Figure 4 shows the distribution of determined insoluble residues by percent intervals. More than 50 percent of the samples fell in the intervals between 0 and 10 percent.

The ternary plot in Figure 5 shows the percentages of insoluble residue, calcite and dolomite of a sample by a single point. The amount of each constituent in a sample is proportional to the perpendicular distance from the point to the side of the triangle opposite the constituent. For example, point A in Figure 5 represents a sample containing 42 percent insoluble residue, 49 percent calcite, and 9 percent dolomite.

Thin-Section Descriptions. --Thin sections were made from 79 of the samples including both expanding and nonexpanding rocks. Study with the petrographic microscope indicates that, based on mineralogy and texture, four major types or end members can be distinguished. These are listed in the following together with a discussion of the predominant characteristics observed in each group. Photomicrographs of each type are shown in Figure 6.

1. Well-crystallized dolomite. These rocks consist principally of interlocked dolomite grains with distinct grain boundaries and little calcite or insoluble material between dolomite crystals. In the whole group the dolomite crystal size ranges from about 10 to 60 μ, but in any one example the grain size is nearly constant. Primary sedimentary features are generally not visible and the insoluble residue content of these rocks is low.

2. Micrograined calcite. Individual calcite grains in these sections, aside from recrystallized veins or patches, are predominantly very fine grained, ranging from nearly submicroscopic to about 5 μ. Variations within this dense fabric are due to variations in the aggregations of these grains. Fossils, oolites, pellets, and transported fragments are the most common of these aggregations. When distinct aggregations are not evident, the extremely fine-grained calcite produces a very dense fabric almost devoid of primary sedimentary features. Insoluble content ranges from less than 1 to 50 percent.

3. Calcite and dolomite in discrete zones. Thin sections of banded or laminated rock types may show the boundaries that separate layers dominantly dolomite from those dominantly calcite. These boundaries may be gradational or abrupt in character. Many of the abrupt or sharp boundaries are marked by the presence of stylolites. Within the layers the character of the material closely resembles that described in 1 and 2 .

4. Interspersed calcite and dolomite. Discrete, well-crystallized dolomite rhombs, surrounded by finer-grained calcite, are characteristic. The dolomite grains appear clear or zoned with inclusions in thin section. The calcite, because of its finer grain size and because the insoluble materials are concentrated in this fraction, is usually cloudy or dark in color. These rocks are characteristically high in insoluble residue.

RESULTS OF TESTS FOR REACTIVITY

Expansion

From each of the samples collected one prism was made and tested by the method developed by Hadley (5) for measuring the alkali-induced expansion of carbonate rocks.

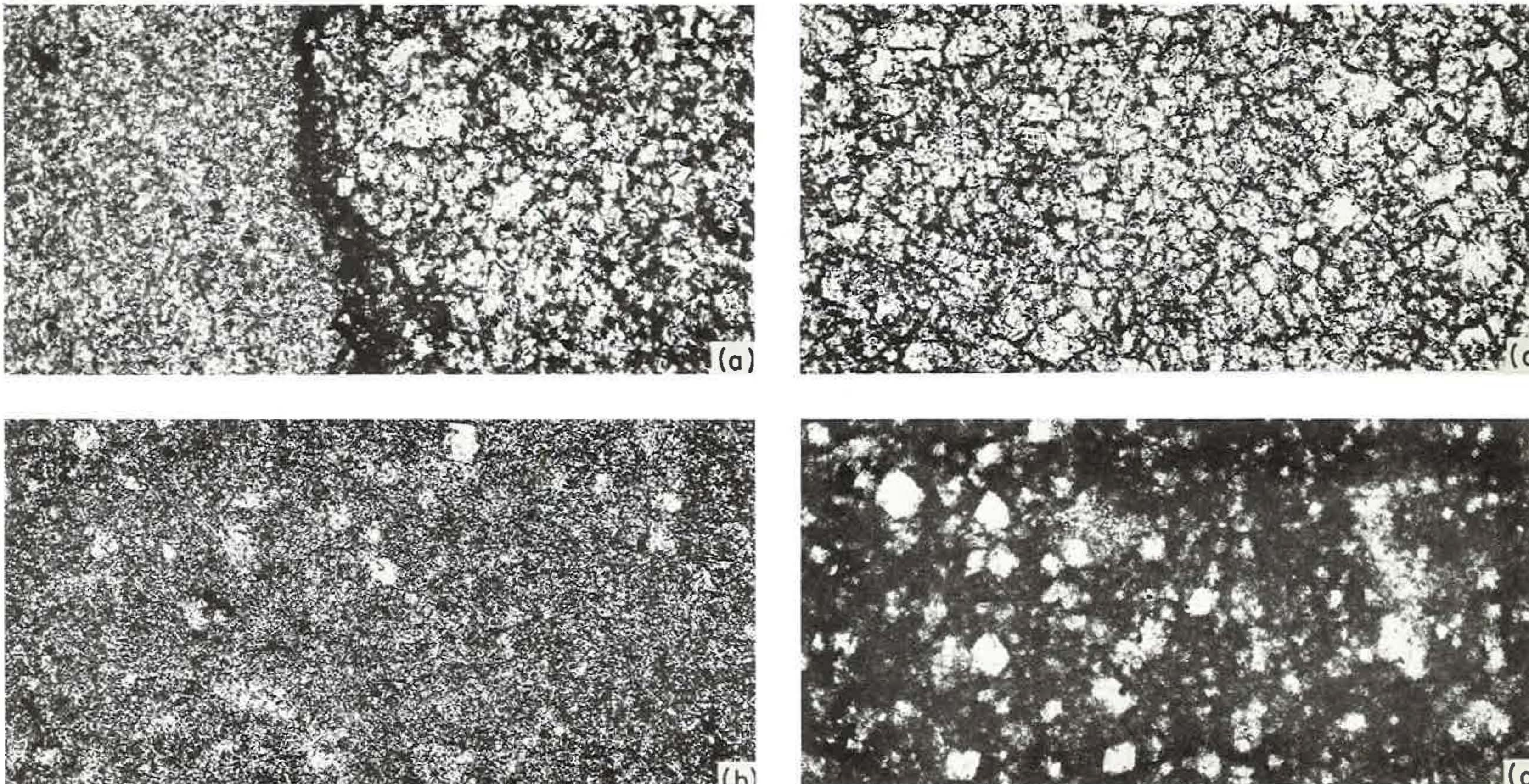

Figure 6. Photomicrographs (50X) of typical Virginia carbonate rocks: (a) medium-grained, well-crystallized dolomite with no primary sedimentary features evident; (b) fine-grained calcite with sizeable amounts of clay and clay-size quartz intermixed and a few recrystallized patches evident; (c) laminated rock with alternating zones of fine calcite and coarse dolomite and sharp boundary more prevalent than gradational types; and (d) discrete dolomite rhombs surrounded by matrix of fine-grained calcite and clay.

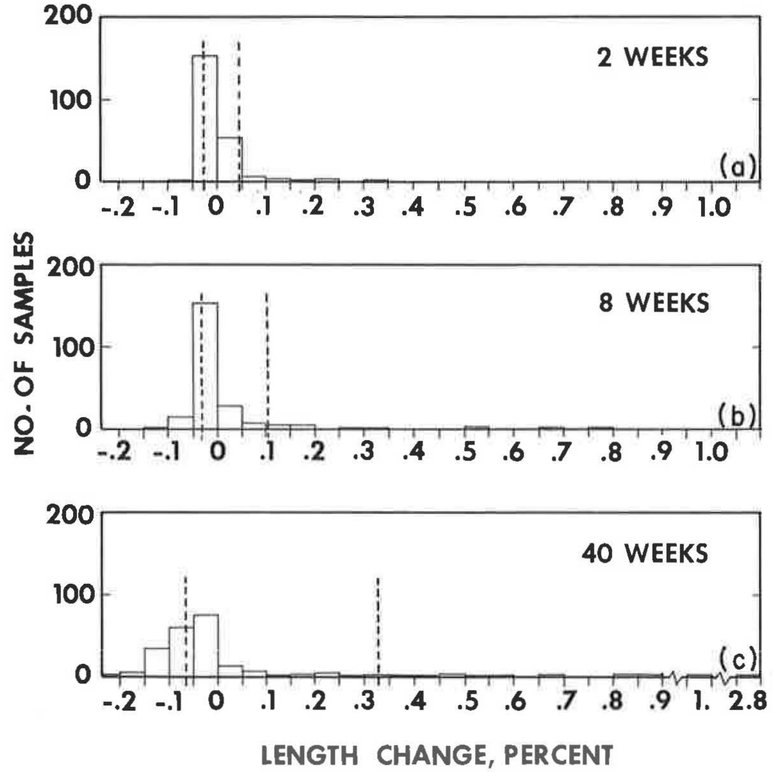

Figure 7. Number of samples vs length change at 2, 8, and 40 wk for 224 test samples. Vertical dashed lines represent average expansion and contraction.

The procedure involved cutting 1¼- by ¼- by ¼-in. prisms normal to the bedding from the rock samples and grinding conical apices on each end. The prisms were measured in a length comparator, soaked in distilled water until they reached equilibrium length and transferred to a polyethylene bottle containing 30 ml of 1.0 N NaOH solution. The prisms were removed and measured at 1-wk intervals up to 8 wk, and at 4-wk intervals thereafter.

Results of the prism measurements are shown graphically in Figure 7a, b and c for ages of 2, 8, and 40 wk, respectively. Several important aspects of length change are brought to light in these graphs; (a) the length changes, whether expansion or contraction, are progressive with time; (b) average expansion is nearly an order of magnitude greater than average contraction at ages of 8 wk or greater; and (c) the total number of rocks that contract in the NaOH solution is much greater than the number that expand.

Figure 8 shows the expansion curves of two typical samples each from those rocks showing very high, high, and moderate expansions. The general shape of the individual curves seems to indicate that expansion in most cases can be detected at soaking times of 2 to 4 wk. Expansion measurements taken to an age of 12 mo yielded only a few prisms in which expansion began after 4 wk in NaOH.

As length change data accumulated, it became evident that more intensive testing of certain quarries was needed. This work is now in progress. Detailed sampling of all beds for prism tests and hand picking and crushing of selected beds for fabrication of concrete test samples have been accomplished for several quarries. Results of this work to date have substantiated the results of the original survey. Prism expansions of up to 6.5 percent with no visible cracks at 30 wk and concrete expansions in excess of 0.1 percent at 1 yr have been obtained for this material.

The status of the prism test (5) should be emphasized at this point. At present, it is not an accepted test by any standardizing agency but is one of several currently

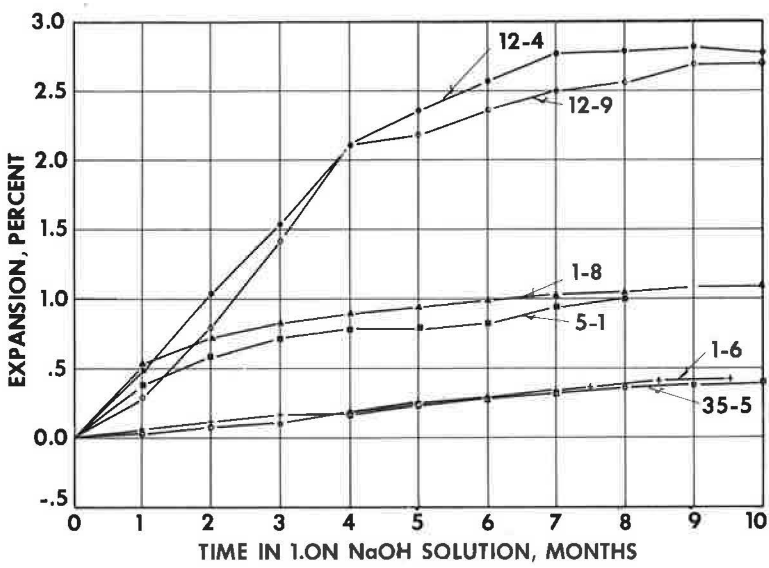

Figure 8. Representative expansion curves.

under investigation. Investigations, directed toward correlating the prism test with concrete behavior and especially toward determining a threshold point for deleterious reaction, are under way. Consequently, prism test results should be viewed at this time in a relative rather than an absolute sense.

Rim Formation

In addition to the expansive alkali-induced reaction, rim growth in concrete aggregates is of current interest. Bisque and Lemish (1, 2, 3) first noted rims or silica-rich zones in the aggregate particles near the aggregate—cement paste interface of some Iowa concretes. These rims appeared in positive relief when the concrete was sawed and etched in hydrochloric acid. Subsequently Mather et al. (7) described rims in concrete aggregates which are frequently discolored and which are preferentially etched in acid and appear in negative relief.

To investigate the tendency of Virginia aggregates to form rims, ½-in. cubes were cut from all of the 224 samples under study. These were embedded in mortar bars, conforming to the requirements of ASTM C 227, with cement having an alkali content of 0.95 calculated as equivalent Na_2O. The bars were stored in closed containers over water at a temperature of 37.8 ± 1.7 C. After 8 wk, each mortar bar was sawed parallel to its length so that each half contained one-half of each of the embedded cubes. One of the sawed surfaces was etched in 3 N HCl. Rims were found in 25 of the 224 cubes. All but two of these were negative rims. The composition of the rim-forming rocks and the type of rims formed can be seen in Figure 9. Figure 10 shows a negative and a positive rim from this group.

The distribution of the rim-growing samples in the composition plot in Figure 9 shows that: (a) the negative rims are virtually limited to high calcite rocks, (b) the insoluble residue contents are generally low, and (c) the limited evidence in the case of positive rims points to compositions high in dolomite. A check for rim vs expansion showed that six of the 25 rimmed rocks also expanded, and that two of these reached expansions in excess of 0.1 percent after 6 mo. Because the percentage of the rim-growing rocks that expanded is about the same as the percentage of all the samples that expanded, no relationship between rim growth and expansion appears to exist. It should be noted also that no effects, either deleterious or beneficial, have been proven attributable to rim growth at this time.

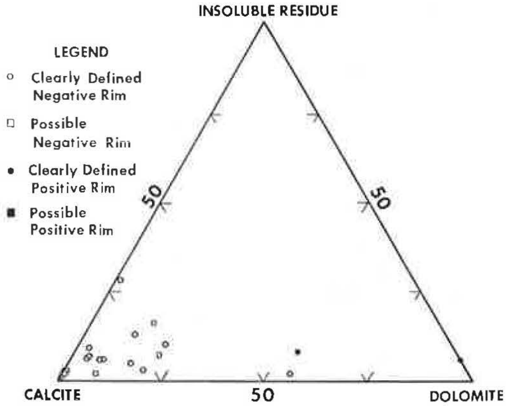

Figure 9. Composition of rim-forming rocks.

RELATIONSHIPS OF REACTIVITY TO COMPOSITION AND STRATIGRAPHY

An understanding of the relationships between expansive alkali reactivity and other intrinsic properties of carbonate rocks is essential to an understanding of the fundamental cause of the observed deleterious reaction. Figures 11 and 12 were plotted to determine whether any relationship exists between expansive reactivity and either carbonate mineralogy or insoluble residue content. The number of samples of a given composition is plotted as in Figures 3 and 4 along with a superimposed dashed line showing the number of samples of that composition which expanded in the prism test.

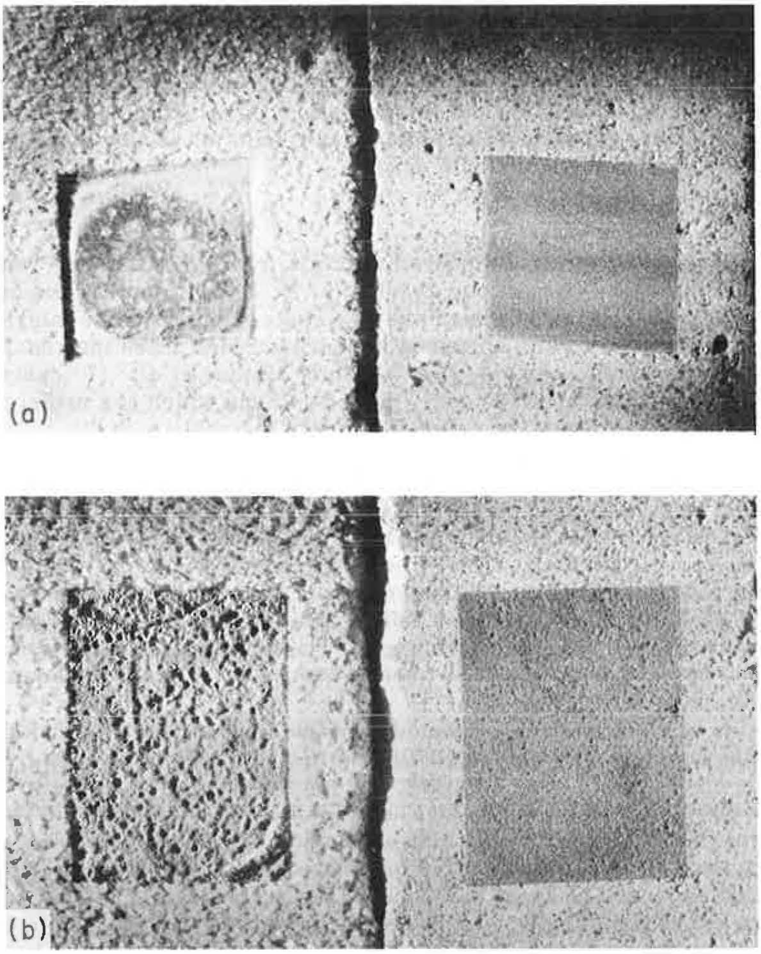

Figure 10. Close-ups of sawed cubes in mortar bars comparing acid-etched and non-etched halves: (a) negative rim, and (b) positive rim.

The correlation of expansion with certain intermediate mixtures of calcite and dolomite appears fairly good in Figure 11. A puzzling aspect of the distribution of expanding samples in Figure 11 is the lack of such samples in the rocks composed of 70 to 90 percent dolomite in the carbonate fraction. Of those rocks in the 10 to 70 percent dolomite range, 42.7 percent expanded, compared to only 6.7 percent in the 0 to 10 and 70 to 100 percent dolomite ranges. The correlation between expansive rock and insoluble residue percent shown in Figure 12 may be even more significant. Those rocks containing 15 to 35 percent insoluble residue have a much higher percentage of expanding prisms than do those outside of these limits.

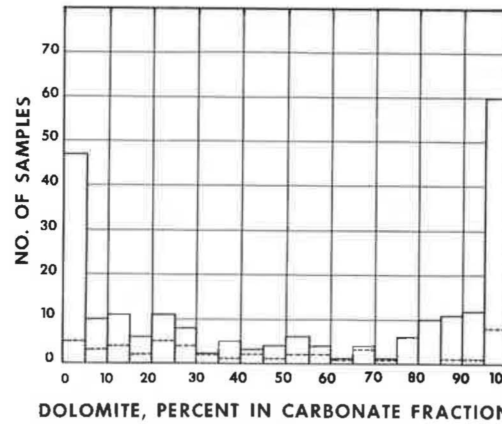

Figure 11. Distribtuion of calcite and dolomite contents of all samples. Number of rocks within each interval which expanded in the prism test is indicated by dashed line.

From the standpoint of total composition, a more comprehensive view of the relationship of expanding samples to all the samples tested is evident in the ternary diagrams in Figures 13, 14 and 15. Figure 13, like Figure 5, shows the ternary composition of each of the 224 test samples. In addition to the compositions, the diagram indicates the samples that expanded in the prism test in contrast to those that either contracted or remained constant. Figure 14 shows the compositions of those samples which expanded more than 0.2 percent at 6 mo. This 0.2 percent figure was arbitrarily adopted as a value large enough to cause

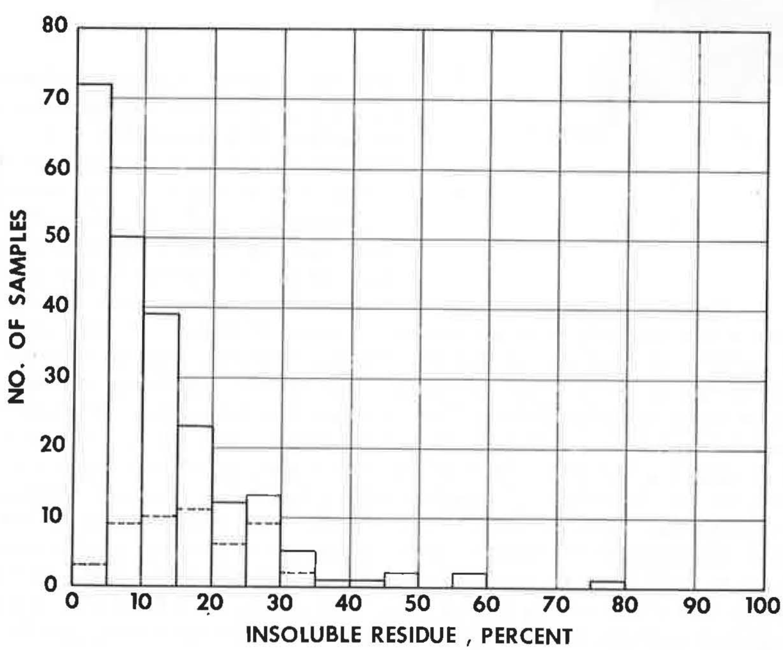

Figure 12. Insoluble residue contents of all samples. Number of samples within each interval which expanded in prism test is indicated by dashed line.

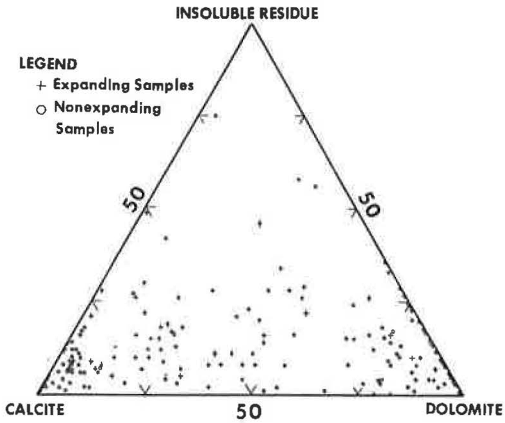

Figure 13. Three-component diagram of 224 test samples, showing which samples expand in the prism test at 6 mo and which did not.

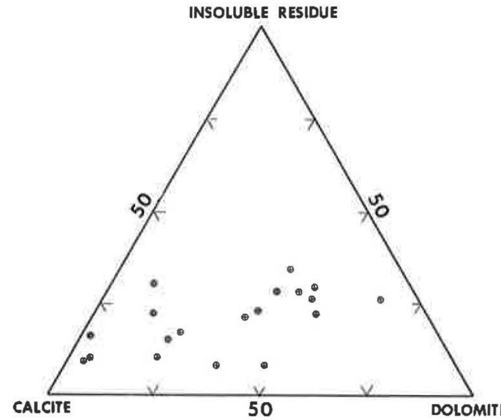

Figure 14. Composition of all samples under test which expanded 0.2 percent or more at 6 mo.

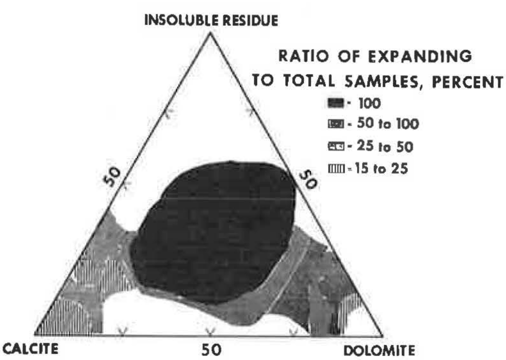

Figure 15. Contoured diagram of distribution of ratios of expanding samples to total samples, determined for 400 equal area increments of ternary plot.

TABLE 3

DISTRIBUTION BY FORMATION OF ROCK SAMPLES EXPANDING MORE THAN 0.2 PERCENT AT 6 MONTHS

Period	Formation or Member	No. of Samples	Quarries Involved
Mississippian	Newman Seam	1	1
Ordovician	Lowville (Moccasin)	4	2
	Edinburg (Athens)	3	2
	Beekmantown (Upper Black Beds)	11	3
Cambrian	Shady (Tomstown)	1	1

concern. Table 3 gives the distribution by formation of the samples that expanded more than 0.2 percent at 6 mo. From this tabulation it is evident that the most reactive material is concentrated in three stratigraphic units, the Lowville, Edinburg and Upper Beekmantown all of Ordovician age. It is interesting to note that most of the reactive rocks reported to date from other areas have been from Ordovician strata. Figure 15 is a contoured plot showing the composition field for various percentage values of reactive samples in the total samples falling in that portion of the diagram. The ternary field was divided into 400 equal increments using standard triangular coordinate graph paper. Counts were made in the 400 small triangles formed by the 5 percent lines. Points on a line were counted in both triangles sharing that line. The percentage of samples showing expansion was plotted based on the total number of samples falling in each increment. From this figure, it would appear that there exists a certain area in the three-component field representing rocks most likely to expand. The variations in frequency of occurrence of the expanding rocks, which occur in the area between the field of maximum value and the corners for pure calcite and pure dolomite, may or may not be real. Lack of a sufficient number of samples or the use of too fine a grid may be responsible for this apparent anomaly.

SUMMARY

This paper presents the results of various tests on carbonate rock samples taken during a survey of carbonate aggregate sources in Virginia. It was made to determine the carbonate rock types produced in Virginia, the distribution of these rock types, and the possible extent of the problem of alkali reactivity. Based on the results of prism tests in which only 20 samples expanded greater than 0.2 percent at 6 mo, it appears that alkali-carbonate reaction is at present a problem of limited rather than major proportions in Virginia. However, the occurrence of rocks that expand as much as 6.5 percent in the prism test and greater than 0.1 percent in concrete indicates that in specific areas the problem is such as to cause concern.

The composition of reactive-carbonate aggregates from Virginia appears, from the limited data presented, to exhibit certain clearly defined trends. Intermediate calcite and dolomite percentages in the carbonate fraction and high insoluble residue contents are characteristic. From the standpoint of stratigraphy, the reactive samples were concentrated in three formations, Beekmantown, Edinburg and Lowville, all of Ordovician age.

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