

Carbonate Aggregate Reactions: Recent Studies and an Approach to the Problem

JOHN LEMISH and WILLIAM J. MOORE, Iowa State University, Ames

The results of some recent studies on carbonate aggregate reactions are presented and the approach to the problem of deleterious behavior of certain varieties of carbonate rocks in concrete through a systematic study of highway concrete is described.

Expansion studies were made on a variety of carbonate rocks occurring in Iowa. Data obtained from the alkali-expansion test of carbonate rocks were classed into four categories similar to those of Newlon and Sherwood: (a) A few rocks with expansion greater than 0.5 percent; (b) Some rocks with expansion between 0.0 - 0.5 percent; (c) A few rocks with reversed behavior—a preliminary contraction followed by expansion not exceeding 0.5 percent; and (d) The majority of the rocks which contracted. Quantitative calcite-dolomite X-ray diffraction analysis of the rocks involved in expansion studies indicates that the rocks containing dolomite dedolomitize to some degree in alkaline solutions regardless of whether they expand or contract (Table 3). Preliminary studies show that an apparent relationship may exist between the amount of expansion (or contraction) and the initial effective porosity. Rocks with higher effective porosities (> 8%) contracted; those with lower effective porosities (8% or less) expanded. The results to date favor a causative mechanism of expansion most closely related to rock texture and pore structure of the rock.

Additional research on the effect of the reaction environment (method of inducing the reaction) on the behavior of silica was studied by embedding cores of selected aggregate in 2- by 4-in. mortar cylinders and then reacting the cylinders in a series of environments including: (a) autoclaving at 220 F for 1 week; (b) hot water bath at 55 C for 3 months; (c) storage at high humidity at 55 C for 3 months; (d) storage at high humidity at room temperature for 1 year; and (e) paraffin coated, storage over water of room temperature for 1 year. The results (Table 4) indicate that rocks react in all environments and the degree of reaction varies with intensity of the environment. The importance of moisture is also emphasized. The rocks show a relative gain in silica (insoluble residue) content for environments a, b, and c. All rocks show a relative decrease in environments d and e. For comparative purposes one could consider that natural non-winter environment of highway concrete to approximate in part the range of experimental environments b, c, and d. The work suggests that in future studies attention should be paid to the method of inducing reaction in carbonate rocks.

An approach to the problem of why certain carbonate aggregates are related to distress in concrete has been undertaken through a study of highway concrete in order to learn more about the change in the entire system: coarse aggregate, and the fine aggregate-cement paste matrix. A chronological sequence of cores was taken from concrete highways with good service records made from the same coarse aggregate and this was also done with concretes having poor service records. Some cores of the same age but showing variation in concrete condition related to variation in aggregate were also taken. Systematic X-ray diffraction, chemical, and petrographic techniques are being used to study the matrix and coarse aggregate of the concrete. The sonic modulus and compressive strengths of the cores are also being measured as part of the program. It is hoped that this study of concretes of varying ages with good and poor service records will provide: (a) a basis for understanding how rocks contribute to distress in concrete; and (b) better knowledge of the "changes" or "aging" which occurs in concrete. Such information is essential to establish the causative mechanism(s) of distress.

•CONSIDERABLE interest exists concerning the general problem of behavior of carbonate aggregates in concrete. A principal objective of researchers in this area is an understanding of how carbonate rocks contribute to distress in concrete. Although progress has been made (i. e., recognition of expansive carbonate rocks) through the contributions of many, attainment of this objective will require more research in several areas. Two principal areas are (a) continued research on the reactivity of carbonate rocks having differing properties and service records in alkaline (high pH) environments, and (b) a broader and more integrated view of the various aspects of the problem as it exists in different parts of the country.

The purpose of the first section of this paper is to review recent studies on alkali reactivity of carbonate rocks and present additional data on this subject. The specific areas are (a) expansion studies, and (b) environmental effects on carbonate reactions.

In the last section of the paper a brief summary of some aspects of the problem of carbonate aggregate behavior in Iowa is given to provide an understanding of the current research effort on the "aging" of highway concretes with both good and poor service records.

EXPANSION STUDIES

This study was undertaken on a variety of carbonate rocks occurring in Iowa to determine their expansion behavior by techniques used in similar studies by Swenson and Gillott (1), Hadley (2), and Newlon and Sherwood (3). Another purpose of this study was to investigate the feasibility of applying the relatively simple techniques required in conducting expansion studies as a possible new test for evaluating carbonate rocks.

Rocks Sampled

The carbonate rocks utilized were obtained from 9 quarries in central and eastern Iowa (Table 1). An additional sample of rock from Virginia was supplied by W. Cullen Sherwood of the Virginia Council of Highway Investigation and Research. In selecting the rocks an attempt was made to secure a variety of carbonate rocks with differing lithology and service records. The rocks currently considered to have good service records when used in highway concrete are those from the Dubuque, Linwood (except for beds 16 and 17, Solon Member), River Products, and Ferguson (beds 11-16 only, Eagle City Member) quarries. Rocks with poor service records are those from the Earlham, Glory, and LeGrand quarries. The Douds and Otis quarries are considered in a doubtful category as far as service record is concerned and recently serious consideration has been given to stop further use of Otis stone in highway concrete.

TABLE 1
QUARRIES SAMPLED

Quarry	Location	Geologic Age	Stratigraphic Position	Beds Sampled ¹
Douds	Douds, Van Buren Co.	Middle Miss.	St. Louis Fm.	6, 7A, 7B, 8A, 10A, 10B, 11A, 11B, 12
Dubuque	Dubuque, Dubuque Co.	Middle Ordovician	Prosser member, Galena Fm.	1, 3, 4
Earlham ²	Earlham, Madison Co.	Upper Penn.	Bethany Falls member, Swope Fm.	4, 5, 6
Ferguson	Ferguson, Marshall Co.	Lower Miss.	Eagle City and Maynes Creek ³ member, Hampton Fm.	2 ³ , 4 ³ , 6, 7, 9, 10, 11, 12, 13, 14, 15, 16, 17, 19
Glory ²	Blackhawk Co.	Upper Devonian	Rapid member, Cedar Valley Fm.	2, 3, 4, 5, 6, 8, 9, 10
LeGrand ²	LeGrand, Marshall Co.	Lower Miss.	Maynes Creek member, Hampton Fm.	8, 9, 10, 11, 12, 13
Linwood	Buffalo, Scott Co.	Middle Devonian	Otis and Davenport members, Wapsipinicon Fm.; Solon ³ member, Cedar Valley Fm.	3, 4, 6, 9, 10, 11, 13, 14, 16 ³ , 17 ³
River Products	Iowa City, Johnson Co.	Upper Devonian	Coralville member, Cedar Valley Fm.	1, 4, 6
Otis ²	Cedar Rapids, Linn Co.	Middle Devonian	Otis member, Wapsipinicon Fm.	2, 3, 6, 8A, 8B

¹ Bed numbers as shown correspond with stratigraphic sections on file at the Iowa State Highway Commission with the exception of the Linwood quarry.

² No longer used as aggregate source.

³ Denotes member samples occur in.

Sample Preparation

The samples were prepared from a representative slab of rock taken from individual beds in the nine quarries. Two flat surfaces parallel to bedding and 2 in. apart were cut on each slab. Cores $\frac{1}{2}$ in. in diameter and 2 in. in length were rapidly drilled normal to bedding with a diamond bit mounted on a drill press. Six cores were taken from each block according to a pattern in which the cores were spaced at approximately 1 in. centers around the perimeter of a 45° triangle. The three cores located at the vertices of the triangular pattern were pulverized and thoroughly mixed to provide a sample for wet chemical and X-ray diffraction analysis. The three cores located at the midpoint of each side were used for expansion measurements after 45° tapers were ground at the ends with an emery wheel.

Experimental Methods

Each sample was analyzed for its major chemical constituents, initial dolomite content and initial effective porosity. Two cores from each bed were immersed in solutions of 1.0 normal sodium hydroxide; a third was stored in distilled water as a control. Length changes were measured for periods of up to 7 months. At the end of this period certain samples which displayed characteristic behaviors in the alkaline solution were selected for further studies. Additional parameters considered were macroscopic and microscopic textural features, acid-insoluble residue composition, final dolomite content, and final effective porosity.

The wet chemical analyses for calcium, magnesium, silicon and insoluble residue of each sample were determined according to the method of Bisque (4).

Initial and final dolomite contents were determined by a quantitative X-ray diffraction technique according to the method of Handy (5). A General Electric diffractometer incorporating a scintillative counter and pulse height discriminator was used. Peak intensities were measured by cumulative counting across the peaks during a 20 scan with

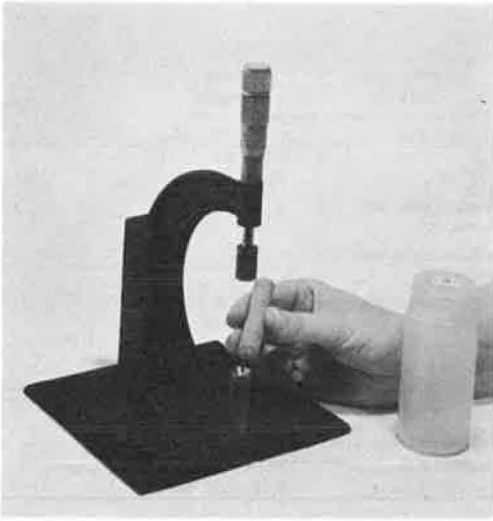


Figure 1. Specially adapted micrometer gage adjacent to a tapered core of rock and polyethylene bottle containing alkaline solution.

the count total being automatically printed out at the end of the scan. Samples were ground to a particle size of less than 1 micron in a vibratory impact grinder. The sample mounts were packed under a standard pressure of 1,000 psi and rotated during the scan to detect any preferred orientation effects. A calibration curve was prepared from calcite-dolomite mixtures varying by 10 percent increments over the range of 0-100 percent.

Effective porosities were calculated from data obtained with a Ruska mercury capillary apparatus.

The measurement of expansion of the cores was made with a mounted micrometer with end plugs (Fig. 1) which accepted a 45° taper. The instrument was calibrated with a 1.760-in. invar steel cylinder. The three expansion cores were stored for 24 hr in 150 ml of distilled water before an initial length reading was recorded. Following the initial reading, two cores were transferred to individual airtight polyethylene bottles containing 150 ml of 1.0 normal sodium hydroxide.

The third was left in water as a control.

Before each measurement the cores were rinsed in distilled water and surface-dried. Four readings for each core were obtained by rotating through 90° steps in the micrometer. Readings were reproducible within 0.001 in. and expansion expressed as percent of initial length agreed within 0.025 percent for duplicate cores.

Textures were studied by means of polished sections using a reflecting microscope.

Experimental Results

Expansion.—The data on all the samples from nine quarries are presented in Table 2. The insoluble residue, calcium, magnesium, and silicon contents are presented with the expansion data obtained after 150 days in sodium hydroxide solution.

On the basis of rate and extent of expansion after an arbitrarily chosen period of 150 days, it was possible to assign the samples studied to one of four categories:

- Category I—samples which expanded in excess of 0.5 percent.
- Category II—samples which expanded between 0.0 and 0.5 percent.
- Category III—samples which contracted prior to expanding.
- Category IV—samples which contracted steadily.

Data pertinent to these samples are presented in Table 3 and in Figures 2-9. The sample numbers used in Table 3 are also used in Figures 2-9 to facilitate graphical presentation.

Relationship of Expansion to Bedding Plane Orientation.—The expansion results plotted in Figures 2-5 were obtained from samples cut length-perpendicular to apparent bedding features. It was necessary to determine what effect planes of weakness such as clay seams may have had on the observed expansion. Six of the original bedding plane slabs from the Glory quarry were used. In this instance samples were cut length-parallel to bedding. Expansion results over a period of 75 days are presented in Figure 6. The prime superscript aids comparison with corresponding samples in Figures 2-4. Specimens cut normal to bedding expanded considerably more than those cut parallel to bedding.

Texture.—Hand specimens for each sample included in Table 2 were described as medium to tan to gray, finely crystalline dolomitic limestones. Many appeared to be

TABLE 2
ANALYSES OF ROCK PRIOR TO ALKALI TREATMENT
AND EXPANSION DATA

Quarry	Bed	Residue Wt. (%)	Ca as CaCO ₃ Wt. (%)	Mg as MgCO ₃ Wt. (%)	Si as SiO ₂ Wt. (%)	Expansion ¹ (%)
Doud	6	2.8	95.3	1.5	1.9	-0.1
	7A	8.3	56.8	32.9	5.7	0.0
	7B ²	11.6	49.9	36.8	7.9	0.2
	8A	2.7	96.6	0.4	1.5	-0.1
	10A	22.9	44.0	31.6	19.7	-0.2
	10B ²	14.5	66.6	17.0	10.2	0.4
	11A	2.6	57.8	39.4	1.6	0.0
	11B	2.6	54.4	41.2	1.9	-0.1
	12	4.4	64.8	29.3	2.8	0.0
	Dubuque	1	3.5	92.9	3.0	3.1
3		15.5	45.0	38.8	12.9	-0.2
4 ²		3.3	51.6	44.3	2.3	-0.2
Earlham	4	13.4	81.3	3.6	12.1	-0.1
	5	7.3	88.0	3.8	6.3	-0.1
	6 ²	26.7	61.0	10.5	21.0	1.2
Ferguson	2	1.8	89.3	9.0	1.7	-0.1
	4 ²	7.1	52.6	38.6	5.2	-0.1
	6	0.8	93.8	5.3	0.6	-0.1
	7 ²	11.2	50.6	36.1	7.5	0.1
	9	1.6	71.3	23.9	0.4	-0.2
	10	2.7	63.0	33.2	2.1	-0.1
	11	3.2	62.0	33.4	2.1	-0.1
	12	1.9	95.1	2.2	1.7	-0.1
	13	2.8	64.8	31.2	1.9	-0.1
	14	1.4	78.8	18.3	1.1	-0.1
	16	1.3	89.0	8.6	1.7	-0.2
	17	1.4	78.3	19.1	1.7	-0.2
	19	1.9	59.9	36.5	1.2	-0.2
Glory	2 ²	7.2	66.5	24.8	5.2	0.8
	3 ²	10.1	65.2	23.4	6.8	1.2
	4 ²	10.9	60.9	26.1	7.5	0.4
	5 ²	12.1	61.9	23.9	8.6	1.1
	6 ²	12.8	62.9	22.1	9.2	0.8
	8 ²	9.1	68.4	20.7	6.9	0.2
	9	15.9	53.3	28.4	11.2	0.0
	10 ²	16.1	50.3	31.5	11.7	0.1
LeGrand	8	2.7	57.4	37.7	1.9	0.0
	9	2.6	56.1	39.0	1.9	0.0
	10	1.6	70.3	26.3	1.5	0.0
	11	1.6	64.1	31.9	1.6	0.0
	12	2.0	62.0	34.1	1.7	0.0
	13	1.0	82.0	15.0	1.3	0.0
Linwood	3	0.4	97.0	1.9	0.6	-0.1
	4	0.8	98.3	0.4	0.7	-0.1
	6	0.7	97.1	1.6	0.3	-0.1
	9	1.2	96.8	1.6	0.9	-0.2
	10	0.0	97.3	1.5	1.3	-0.1
	11 ²	6.4	78.8	13.3	1.6	-0.2
	13	2.4	91.8	5.1	1.7	-0.1
	14	0.9	96.8	1.2	1.2	-0.2
	15	2.6	85.5	9.9	1.9	-0.1
	16	3.7	89.3	5.5	2.6	0.0
	17 ²	9.7	76.3	11.0	7.7	0.5
Otis	2	1.6	77.5	19.0	2.0	-0.1
	3	1.2	53.0	44.9	1.0	-0.2
	6	1.7	53.3	43.6	1.3	-0.2
	8A	0.2	52.8	45.7	0.8	-0.3
	8B	0.3	52.6	44.4	0.2	-0.2
River Products	1	0.1	95.0	5.1	0.5	-0.3
	4	0.3	96.6	2.3	0.4	-0.2
	6	1.9	97.9	2.2	1.0	-0.1

¹150 days in NaOH.²Denotes samples selected for further study (see Table 3).

TABLE 3
CARBONATE ROCK DATA

Sample No.	Quarry and Bed	Residue Wt. (%)	Dolomite ¹ Wt. (%)		Dolomite Reacted Wt. (%)	Expansion After 150 Days (%)
			Initial	Final		
(a) Category I - Expansion Greater than 0.5%						
1	Earlham-6	26.7	24	11	54	1.21
2	Glory-3	9.9	62	32	44	1.18
3	Glory-5	11.0	66	42	36	1.05
4	Virginia 1s	25.1	70	64	9	0.97
5	Glory-6	13.2	63	54	14	0.83
6	Glory-2	6.1	54	39	29	0.77
(b) Category II - Expansion Between 0.0-0.5%						
7	Linwood-17	9.7	21	4	81	0.45
8	Doud-10B	14.5	77	32	59	(0.38) ²
9	Glory-8	9.6	45	24	47	0.21
Average 41						
(c) Category III - Expansion Preceded by Contraction						
10	Glory-4	10.8	52	46	12	0.39
11	Doud-7B	11.6	87	58	33	(0.15)
12	Ferguson-7	11.4	89	82	8	0.12
13	Glory-10	16.2	84	61	27	0.11
(d) Category IV - Steady Contraction (typical samples)						
14	Ferguson-4	7.1	93	93	0	-0.10
15	Dubuque-4	3.3	97	95	2	-0.19
16	Linwood-11	6.4	30	15	50	-0.20
	LeGrand-8	2.7	92	90	2	-0.01
	LeGrand-9	2.6	92	64	30	-0.01
	LeGrand-11	1.6	85	43	49	-0.03
	LeGrand-12	2.0	90	65	28	0.01
	Doud-7A	8.3	80	42	48	-0.01 ²
	Doud-12	4.4	70	17	76	-0.01
	Otis-2	1.6	86	24	33	-0.15 ³
	Otis-6	1.7	98	74	24	-0.23
	Otis-8B	0.3	0.000 ⁴	0.004 ⁴	—	-0.17
	Ferguson-9	1.6	66	45	24	-0.36
	Ferguson-10	2.7	88	67	26	-0.14
	Ferguson-14	1.4	38	28	26	-0.10
	Ferguson-19	1.9	90	33	63	-0.22

¹Dolomite content determined by quantitative X-ray methods (Moore). Represents dolomite content of the rock.

²Samples stored 13 months in sodium hydroxide solution.

³Samples stored 15 months in sodium hydroxide solution.

⁴Calcite: dolomite count ratios.

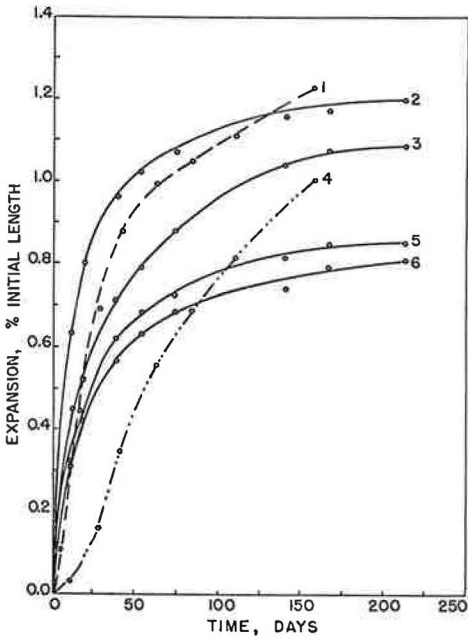


Figure 2. Rate of expansion curves for samples assigned to category I.

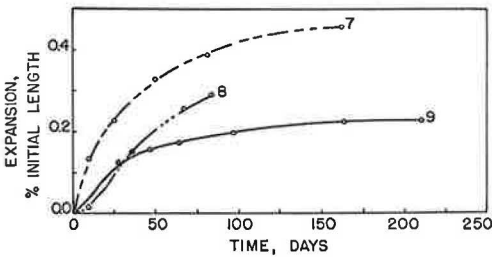


Figure 3. Rate of expansion curves for samples assigned to category II.

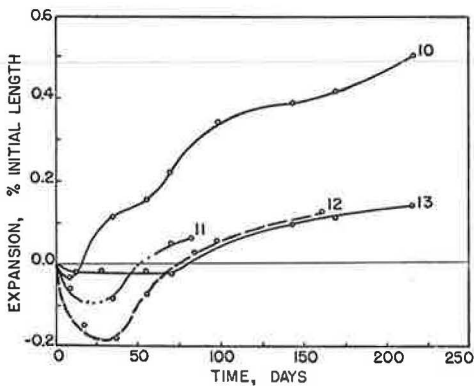


Figure 4. Rate of expansion curves for samples assigned to category III.

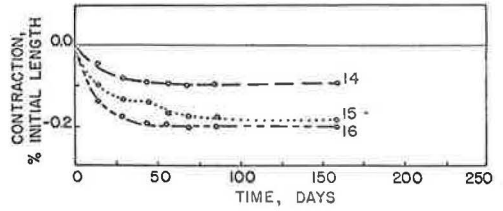


Figure 5. Typical rate of contraction curves for samples assigned to category IV.

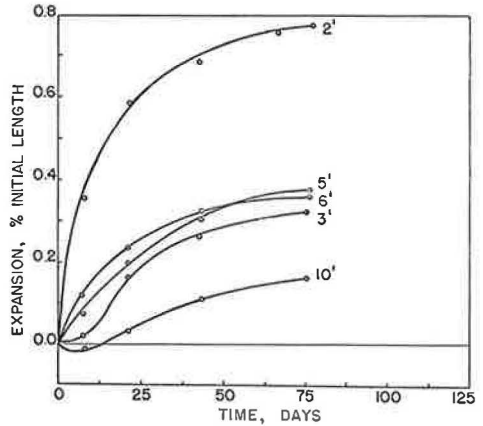


Figure 6. Rate of expansion curves for samples from Glory quarry cut length-parallel to apparent bedding features.

TABLE 4
EFFECTIVE POROSITY OF SELECTED
CARBONATE SAMPLES

Category	Sample No.	Effective Porosity (%)	
		Initial	Final
I	1	7.29	—
	2	7.12	3.66
	3	4.28	3.22
	4	4.25	3.53
	5	5.77	4.08
	6	7.73	3.47
II	9	10.01	3.94
III	10	4.63	3.61
	12	6.63	3.90
	13	13.17	9.23
IV	14	9.27	2.30
	15	9.38	5.75
	Earlham-4	13.47	—
	Glory-9	9.80	5.56

argillaceous. The samples from the Glory quarry were finely laminated. The Earlham-6 sample was an interbedded carbonate-lutite.

Microscopic examination of polished sections showed the samples to consist of varying proportions of: (a) euhedral to subhedral dolomite rhombs 25-75 microns in length; (b) subhedral to anhedral dolomite fragments or irregular crystals averaging less than 25 microns in length; and, (c) a micro crystalline matrix composed of carbonates and clay-sized silicate material. Progressive inspection of samples in category I through category IV revealed a steadily decreasing proportion of small anhedral carbonate fragments. The contracting samples assigned to category IV were characteristically dense, interlocking carbonate mixtures.

Composition of Acid-Insoluble Residue.—Quartz and illite were the only minerals positively identified in the non-carbonate fraction of the samples. Silt to clay-sized quartz was the major constituent of each residue examined.

Effective Porosity.—The initial and final effective porosities of the samples studied in detail are given in Table 4. Several contracting samples not listed in Table 2 have been added. The initial effective porosity has been plotted against expansion in Figure 9.

Discussion of Results

One of the striking observations of the study is that most of the rocks (43) contract slightly and only a few (12) expand. These results and the rest of the data, on the whole, tend to confirm the earlier work of Swenson and Gillott (1), Hadley (2), and Newlon and Sherwood (3). Because of the effective porosity data and additional X-ray diffraction determination of the dolomite contents of samples before and after treatment in NaOH, interpretation of these data has led to some different conclusions which are discussed in the following.

The rate of expansion curves (Figs. 2-5) shows that the relative order of expansion for the rocks tested was established (with two exceptions) after a period of 25 days. This suggests a safe lower time limit for any potential aggregate testing procedure based on relative expansion values. The general tendency for the curves to level off in less than 100 days may be related to a reduction in permeability caused by the accumulation of reaction products in the rock pores. This is inferred from the final effective porosity data given in Table 3.

An explanation for the shapes of the curves in Figures 4 and 5 is not obvious to the authors. Newlon and Sherwood (3) suggest that the apparent contraction may be related to the testing procedure: "The placing of a specimen whose pores are filled with water into a solution of sodium hydroxide may be thought of as creating an osmotic pressure wherein the water tends to migrate from the pores into the solution, slightly dehydrating the specimen and producing a measurable contraction." This explanation appears to be inadequate in the present case because all of the reference samples stored in distilled water showed a similar contraction during the period of measurement; i.e., all the samples contracted in distilled water regardless of their behavior in sodium hydroxide solutions.

The expansion values shown in Figure 6 may be compared with corresponding samples in Figures 2 and 4. It is seen that after 75 days cores cut length-parallel to bedding features have expanded at least one-third less than the length-perpendicular samples. Bedding planes appear to enhance the directional character to the release of stress. Swelling and cracking along bedding planes do not account for the bulk of the observed expansions.

The compositions of samples chosen at random from the 43 which showed contraction are also plotted in Figure 7. Although a bell-shaped curve similar to Hadley's (2) was drawn for comparative purposes through the points obtained from samples which expanded, it is equally apparent that rocks with similar compositions contract. From these data alone it would not be possible to predict expansion on the basis of carbonate composition of the whole rock.

Swenson and Gillott (1) were the first to suggest that the expansion of certain carbonate rocks may be the result of a dedolomitization reaction. Hadley (2) and others (12)

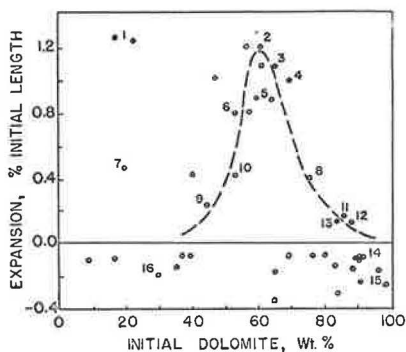


Figure 7. Expansion after 150 days as a function of initial weight percent of dolomite.

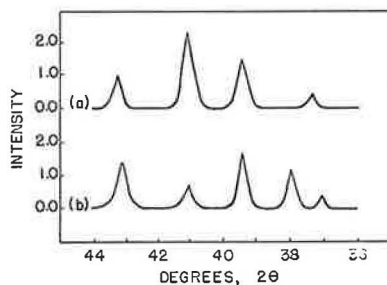


Figure 8. Diffractometer traces of Glory-8 sample: (a) original sample; (b) same sample after residing 200 days in 1.0N NaOH.

concur on this point but as of yet no satisfactory mechanism(s) has been established. Qualitative proof of a dedolomitization reaction is shown in Figure 8. The 38° brucite peak, absent in the "before" trace, appears in the diffractometer trace of a Glory-8 sample after soaking in a 1.0 normal solution of sodium hydroxide for 200 days. The 41° dolomite peak shows an appreciable reduction in intensity, and the brucite peak was the only new reflection observed in any of the "after" samples scanned between 4° and $55^\circ 2\theta$.

The results of a quantitative study of dedolomitization are given in Table 3.

Although the average "percent dolomite reacted" for categories I and II is 15 percent greater than the average value for categories III and IV, it is evident individual specimens which contract indicate up to 76 percent dolomite reacted. From these data it may be wondered if the rate of dedolomitization could ever be dependent on carbonate composition alone. What is most evident in data of Table 3 is the fact that rocks which contain dolomite dedolomitize in alkaline solution regardless of whether they expand or contract.

An additional point of interest observed concerning the data in Table 3 is the strong relationship of insoluble residue content to expanding and contracting rocks. The first three categories of expanding rocks average 13.5 percent insoluble residue. Category IV, the contracting specimens, average 3.1 percent. Workers elsewhere (1, 2, 3) have found a similar relationship. Lemish et al. (7, 8), in earlier work on rim growth studies, have found that the insoluble residue content of a rock is closely related to its ability to grow reaction rims.

It was earlier noted that the sample assigned to categories I and II contained relatively large proportions of small, anhedral carbonate fragments. It would be expected that the rate of dedolomitization should be related to this texture. The average values of Table 2 support this reasoning. These data suggest that the rate of dedolomitization is generally a function of crystal size and not of a specific carbonate composition. Crystal size is an important rate-controlling factor which deserves further consideration.

The observations regarding textural features of the expansive rocks are in complete agreement with those of other workers (1, 2, 3). Because of this agreement, an at-

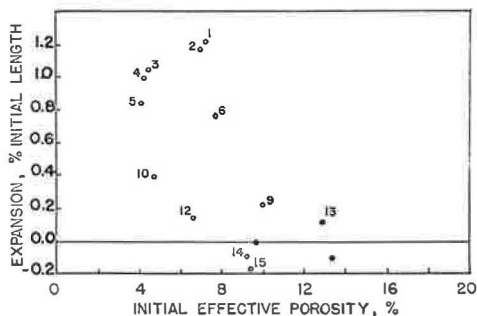


Figure 9. Expansion after 150 days as a function of initial effective porosity.

tempt was made to relate expansion to physical properties of the samples. In the absence of equipment to measure permeability directly, it was decided to compare the samples on the basis of effective porosity.

Figure 9 shows a tendency for those samples assigned to category I to have a relatively low effective porosity. The contracting samples assigned to category IV are characterized by initial porosities greater by at least 60 percent. This suggests a possible causative mechanism for expansion in which the products of a dedolomitization reaction are effective in producing expansion only when the amount of initially available pore space is inadequate to accommodate their rate of accumulation or migration out of the rock.

ENVIRONMENTAL EFFECTS ON CARBONATE REACTIONS

Introduction

During the course of research on carbonate aggregates, several methods of inducing carbonate aggregate reactions related to formation of silicified rims on certain rocks have been employed at Iowa State University and by others elsewhere.

Bisque and Lemish (6) were the first to induce rim growth by either soaking concrete bars at 140 F for 2 months or alternately soaking them at room temperature for a day followed by oven-drying at 140 F for 24 hr. The autoclave (7) has been successfully employed in the University's laboratory to induce reactions in concrete bars rapidly within a matter of hours or a few days. Bisque (8) also grew silicified rims in aqueous environments by immersing blocks of reactive aggregate in sodium metasilicate solutions. Hiltrop (9) originated and Werner (10) extended a reflux procedure to determine rapidly (48 hr) and quantitatively the "silicon" absorption capacities of small rock chips.

Swenson and Gillott (1) induced reaction in Kingston aggregates by reacting concrete bars at 100 percent humidity at room temperature over a period of months. Hadley has adapted the Bisque and Lemish (8) techniques by reacting prisms of rock embedded in mortar bars and sealed in cans at 100 percent humidity at 100 F for 8 weeks.

It is readily understandable therefore when such a variety of environments has been employed to induce reactions, that the influence or effect of environment on the nature of the reaction be seriously considered a problem in interpretation of experimental results.

Another major problem in the quantitative study of reactions is that of sampling. The sampling of aggregate fragments from highway or laboratory-prepared concretes has been difficult and time consuming. Bisque and Lemish removed aggregate samples from a concrete matrix by chipping and filing. Harwood (11) used a dentist drill to obtain his samples for chemical analysis. Gillott (12) used a chisel and dentist drill to study rimmed aggregates found in concrete. The accuracy of such methods is open to question because destructive testing precludes accurate comparisons of "before" and "after" samples.

In view of these problems, a special study was undertaken to investigate the effect of environments on aggregate silicification and to meet the rigorous requirements caused by the use of destructive tests in "before" and "after" samples. A method of providing samples which meets these requirements was devised and applied to evaluate silicification under closely controlled conditions.

Experimental Approach

Bedding plane slabs from the Burton Avenue, Glory, and LeGrand quarries were cut into 8- by 4- by 2-in. blocks for sampling. Cores 0.5 in. in diameter were taken at 1-in. centers over a rectangular grid with a minimum of 20 cores per slab.

Alternate cores from each column and row of a given slab were individually analyzed for silica content using the method of Bisque (4). The remaining cores were embedded in mortar cylinders 4 in. long and 2 in. in diameter. The cylinders were cured for two days at 100 percent relative humidity and 73 F before being transferred to one of five environments:

- Environment A—autoclave (20 psi and 105 C) for one week,
 Environment B—in distilled water at 55 C for three months,
 Environment C—over distilled water at 55 C for three months,
 Environment D—over distilled water at room temperature for
 1 year, and
 Environment E—paraffin-coated cylinders over water at room
 temperature for one year.

Cylinders placed in the autoclave stood on the floor of the steam-filled chamber. The cylinders in and over water at 55 C were individually sealed in polyethylene bottles and submerged in a water bath maintained at that temperature. An evacuated desiccator partially filled with water was used to store the samples in the room temperature environment.

Following the specified exposure to each environment, the cylinders were sawed into disks approximately 0.5 in. thick. The disks were broken by tapping firmly at the periphery. The carbonate cores were removed intact and without residual traces of fine aggregate or hydrated cement paste.

The silica contents of the reacted samples were determined. For each sample the final silica content was compared to the average silica content of its "nearest neighbors" in the original block.

Experimental Results

The change in silica content for the samples reacted in environments A, B, C, D, and E is given in Table 5.

TABLE 5
 EFFECT OF ENVIRONMENT ON REACTION

Sample	Environ- ment ¹	SiO ₂ Wt. (%)		
		Original	After Reaction	Change
Glory	A	11.6	12.5	+0.9
	B	11.2	12.5	+1.3
	C	11.0	11.7	+0.7
	D	12.1	11.2	-0.9
	E	11.7	10.7	-1.0
Burton Ave.	A	3.3	4.4	+1.1
	B	3.0	3.6	+0.6
	C	2.9	3.7	+0.8
	D	3.3	2.7	-0.6
	E	3.0	2.9	-0.1
LeGrand	A	0.9	1.3	+0.4
	B	0.9	1.1	+0.2
	C	0.9	0.8	-0.1
	D	0.9	0.6	-0.3
	E	0.8	0.7	-0.1

¹Environments:

A = autoclave, 20 psi and 105 C for 1 week.

B = in water at 55 C for 3 months.

C = over water at 55 C for 3 months.

D = uncoated over water at room temperature for 1 yr.

E = paraffin coated over water at room temperature for
 1 yr.

Discussion of Results

Two important points which should be emphasized before discussing the results in Table 5 are (a) the reacted samples were recovered quantitatively, and (b) the transfer of silica occurred in the presence of (concrete) pore solutions alone—no bulk/excess water phase was required.

The increase in silica content for the Glory and LeGrand samples is of the same relative order established by Werner (10) using reflux techniques and Bisque (8) with his experiments on chips of rock reacted in ports within mortar bars.

It was earlier noted that rim zones from aggregate fragments reacted in mortar bars were originally separated for analysis by chipping and filing. The representativeness of these samples was questioned (8). In the present work the entire sample was analyzed and no correction is made for the "dilution" effect of unreacted carbonate.

Two important observations can be made from a review of the data given in Table 5: (a) the rocks react in all environments, and (b) the degree and nature of the reaction varies with the intensity of the environment. Although a change in silica content was associated with every environment, the reversal in the silica content related to the environment intensity is of great interest. The rocks show a relative gain in silica content for environments A, B, and C. All the rocks show a relative decrease in environments D and E. Without bulk density data for the specimens before and after the reaction, the actual gain or loss of silica content of the rocks cannot be determined; however, the reversal in the change of silica content does indicate differences in the degree and nature of the reaction as it varies with the environment.

Temperature and moisture are major variables in each environment and it is difficult to state which exerts the greatest effect on the degree and nature of the reaction. Because of previous experience here and elsewhere, the role of moisture is most critical and its importance is emphasized in these experiments.

For comparative purposes, one could consider that natural non-winter environment of highway concrete to approximate in part the range of experimental environments B, C, and D. The work suggests that, in future studies, close attention should be paid to the method of inducing reactions in carbonate rock embedded in mortar.

AN APPROACH TO THE PROBLEM

Recently, as part of the research program on the behavior of carbonate aggregate, a study of highway concretes has been undertaken. To understand this approach, which in essence is a study of how concrete "ages," a brief review of the status of the problem as it exists in Iowa is presented. This is followed by a brief description of the research approach.

Present Status of Problem in Iowa

Although a thorough presentation of the problem is given by Welp and DeYoung (13), some pertinent aspects of it as it is seen today are worthy of review.

The problem can be summarized briefly, as follows: Some rocks fail present acceptance tests and also in service; a few pass present acceptance tests and fail in service; the bulk of the rock used which passes present acceptance tests has a good service record. Rocks with Glory and Earlham characteristics, high insoluble residue dolomites, fail present acceptance tests and are no longer used in service. This would be true of such rocks as the Kingston, Ontario aggregate which is lithologically similar to Glory aggregate in many respects and fails to pass the present ISHC acceptance tests. These reactive and expansive-type rocks are not a present problem and acceptance tests eliminate their use in Iowa.

The aggregates which pass the acceptance tests but have a poor service record are more difficult to categorize. LeGrand rock is an example of this type. Review of service records indicates that rock from the Otis quarry is part of the problem also.

Table 6 was compiled to present some of the similarities and differences of two non-acceptable aggregates related to distress in concrete. Both rocks are dolomitic, contain illitic clay, and have some textural resemblance. In terms of insoluble residue

TABLE 6
PHYSICAL CHARACTERISTICS OF TWO AGGREGATES

Characteristic	Glory Aggregate	LeGrand Aggregate
Texture	Mosaic type	More variable; well-developed crystalline equigranular types predominate; a minor amount of mosaic type occurs
Composition	Calcitic dolomite to dolomitic limestone	Calcitic dolomite
Insoluble residue	Average 12-15%	Average 3%
Clay content	Illitic clay present	Illitic clay present
Reactivity	Highly reactive in concrete environment in terms of rim growth	Slightly reactive in terms of rim growth
Freezing-thawing (water-alcohol) performance	Avg. 30 to 40% loss	Avg. about 4% loss
Silica absorption characteristics	High capacity for silica absorption	Very low capacity for silica absorption
Expansion (soaking rock in alkali)	Expansive—some units expand 1% in 6 weeks	No measurable expansion in 6 weeks time
Dedolomitization (% dolomite reacted)	26 ¹	27 ²
Alkali aggregate reactivity-ASTM-C227-52T (% growth-12 mo)	0.03	0.02

¹ Avg. of 7 samples.

² Avg. of 4 samples.

content, freezing and thawing performance, reactivity and expansion characteristics in hydroxyl-rich environments, the rocks are noticeably different. Although much has been learned concerning the behavior of the various components of carbonate rocks (i.e., calcite, dolomite, clay, quartz) in alkaline environments, the contrast in properties of these unacceptable aggregates makes it difficult to postulate a direct or indirect mechanism(?) by which aggregates cause distress in concrete.

Another major reason for not understanding the true role of aggregate in concrete distress is the lack of knowledge of what happens to concrete as it ages. Study of deteriorated highway concretes and the present observations by Welp and DeYoung on the performance of concrete pavements have indicated certain trends which point to the necessity for more knowledge concerning changes which take place in the entire system: coarse aggregate and the fine aggregate-cement paste matrix.

Current observations indicating certain trends (13) which appear to have validity can be summed up as:

1. Concrete failure due to aggregate presents a wide range of visible physical symptoms (progressive spalling, "D" lines cracking away from joints and cracks, etc.) that are observed in concrete from ages that may range from 2 to 40 years. The overall pattern of distress, once it begins, is similar—regardless of the type of carbonate aggregate used in the concrete.

2. A corollary to this is that there appear to be different kinds of deleterious rock types, each having an effect on the durability of concrete. The rate, amount, and kind of effect depend on the interaction with the rest of the components of the concrete system.

Petrographic study of deteriorated concrete indicates that it is carbonated, soft, contains calcium sulfaluminate, and that most of the original hydrated calcium silicate compounds appear to have been replaced by calcium carbonate. Concrete at the dis-

tressed margins of a slab is chemically and physically a different system than when it was poured.

These observations all indicate the necessity for more knowledge of what takes place in concrete as it ages before the role of coarse aggregate can be evaluated.

Research Approach

The main objective of this phase of research is to learn, if possible, what physical and chemical changes take place in concrete as it ages. Concretes made from the same aggregate but of different ages are the main basis of study. A chronological sequence of cores was taken from concrete highways with a good service record and containing the same coarse aggregate. Two sets of cores representing different ages have been taken from concrete made from Alden stone (pure limestone) and Dubuque stone (dolomite). Similar sets of cores have been taken from concretes with poor service records. A chronological series of cores has been taken from concretes containing LeGrand and Otis stone.

All the cores taken are stored and sampled in a CO₂-free environment. Intervals at 1, 3, and 5 in. from the top of each core are systematically sampled. The matrix and coarse aggregate are separated and analyzed separately.

The following investigations will be carried out in the study: (a) chemical analysis of matrix and coarse aggregate for principal oxides (this includes sodium, potassium, and sulfate contents); (b) X-ray diffraction investigation of the various constituents; (c) petrographic study of thin and polished sections of the concrete; and (d) standard engineering tests—compressive strength and sonic modulus of the cores.

The study is under way at present and all the cores have been taken. Techniques for chemical analyses of matrix and cores have been worked out and systematic analyses have already begun.

CONCLUSIONS

Expansion studies on Iowa rocks produced results similar in most respects to those obtained by others (1, 2, 3). Dedolomitization occurs, to some degree, in dolomite-bearing rocks regardless of whether they expand or contract. This bears out earlier work on compositional variations associated with carbonate reactions—dedolomitization occurs in a high pH environment providing there is access for solutions. The expanding rocks as a whole are argillaceous-appearing dolomitic limestones or calcitic dolomites with fairly high insoluble residues (>7%), fine-grained matrix textures and effective porosities less than 8 percent. Contracting rocks range in composition from pure (low insoluble residue) limestones or dolomites to argillaceous dolomitic types with effective porosities greater than 8 percent. Not enough evidence has been accumulated to postulate a causative mechanism for expansion, but the results to date indicate that in addition to the insoluble residue content, the physical properties of the rock—pore structure and texture—are probably an important factor. Contraction of most carbonate rocks appears to be a definite property which should not be neglected in future work.

Research on the effect of environment on silicification of carbonate rocks indicates that the method by which the reaction is induced controls the intensity of reaction and its overall nature.

A review of the problem of deleterious behavior of certain rocks in Iowa shows they can have a wide range of properties. Study of highway concretes indicates that aggregates are related to the service record and that the pattern of distress appears to be similar regardless of when deterioration commences. Research on the "aging" of highway concrete was undertaken to learn more about the concrete system in the hope that it will provide information on the role of carbonate aggregates.

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