Alkali-Carbonate Rock Reactions in Michigan

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The Michigan State Highway Department has not so far experienced distress of field concrete positively identified as being due to cement alkali-carbonate rock reaction. However, laboratory studies have found three quarried limestones having very mild expansions when incorporated in concrete made with alkali cement. Nineteen other limestones and seventeen natural gravels similarly studied show negligible expansions. Expansion data up to 4 years age are presented for several of the aggregates studied. Two of the limestones which are mildly reactive exhibit dependence of freeze-thaw durability on the alkali content of the cement when the aggregates are placed in the concrete in a vacuum saturated condition. Durability is improved with low alkali cement. The third mildly reactive limestone has not been similarly studied because its freeze-thaw durability even with high alkali cement is good, and it is doubtful that improvement in durability with low alkali cement, if present, could be reliably measured. Deficiencies in the completeness of the present data exist because only portions were produced on a planned research basis. The remainder was obtained as a minor supplement to routine acceptance testing.

•IN 1957 Swenson (1) reported laboratory work on Kingston, Ont. limestone following observation of abnormal expansion in field concrete containing this carbonate rock as coarse aggregate. Expansions were found to be related to alkali content of the cement and were most successfully predicted by observation of expansion bars stored in the ordinary laboratory moist curing room. The simplicity of Swenson's procedure was attractive and led the Michigan State Highway Department Testing Laboratory to make expansion bars on a routine basis simultaneously with concrete batches for freeze-thaw evaluations of aggregates. It seemed possible that potential destructiveness of aggregates, heretofore unidentified as to cause, may have been overlooked and additional data could be acquired rather easily. However, destructive reactions in field concrete have not yet been confirmed in Michigan due either to alkali-aggregate reaction or to alkali-carbonate rock reaction.

Three carbonate rock sources in Michigan give mild expansions with moderately high alkali cement in laboratory moist room storage, but field observations of structures containing these aggregates have not shown adverse effects. Other limestone (as used here, the term limestone refers to rock composed basically of calcite and/or dolomite) sources available to the Michigan market have not shown appreciable expansions in laboratory observation nor have any of the glacial gravels investigated. Of greater perplexity is the observation that two limestones having mild expansion in moist room storage demonstrate considerable sensitivity to cement alkalies in freeze-

Paper sponsored by Committee on Performance of Concrete—Chemical Aspects.

thaw durability tests. Much better durability is developed with low alkali cement. This behavior is similar to that reported by Tremper (2) for certain aggregates in the State of Washington.

TEST PROCEDURES

Expansion bars, 2 by 2 by 11 in. fitted with stainless steel measuring studs, have been made simultaneously with casting concrete prisms for freeze-thaw durability determinations. The procedure used by the laboratory is to make one expansion bar and three 3- by 4- by 16-in. freeze-thaw prisms from each of three batches of concrete made on three different days for each cement-aggregate combination. Thus, three expansion bars and nine freeze-thaw prisms are provided for each evaluation.

The coarse aggregate under test is split into four sieve sizes, $^3/_4$ to 1 in., $^1/_2$ to $^3/_4$ in., $^3/_8$ to $^1/_2$ in., and No. 4 to $^3/_8$ in., recombined into equal amounts of each size and then vacuum saturated and soaked 24 hours prior to incorporating in concrete. The fine aggregate used in all tests was from a single local natural aggregate source, and was regraded to provide the following gradation (percent passing): No. 4 sieve, 100; No. 16 sieve, 70; No. 50 sieve, 17; No. 100 sieve, 2. The concrete is proportioned to contain 5.5 sacks of cement per cubic yard with a 2- to 3-inch slump. The concrete is air entrained using Type I cement with sufficient neutralized vinsol resin solution added to maintain the air at 5 to 6 percent. Freeze-thaw beams are cured under water for 14 days at which time they enter the freezing chamber, using ASTM Method C291, "Resistance of Concrete Specimens to Rapid Freezing in Air and Thawing in Water." Eight cycles of freezing and thawing are obtained per day. Durability factor is computed, based on 300 cycles and a reduction in sonic modulus of 30 percent. Expansion bars are stored in the 73 F moist room immediately after casting, and the molds are removed the following day at which time initial length measurements are taken. Expansion bars remain in the fog curing room and length changes are observed at monthly intervals using a comparator with a 0.0001-in. dial. Corrections of the comparator are made using an invar reference bar.

Strength specimens for 7 and 28 days both in flexure and compression are made from each batch as well as calculation of w/c ratio, weight per cubic foot, etc. To conserve space, the latter data will not be presented unless special interest should develop and make it desirable to do so.

TEST RESULTS

Since the beginning of making expansion bars simultaneously with conducting freeze-thaw evaluations, 17 gravel samples have been studied ranging from very poor to excellent durability. The gravels have been produced using a variety of processing at different sources, ranging from simple washing and screening to heavy media separation, elastic fractionation, or jigs. Most of these glacial gravels originated in the southern peninsula of Michigan but one came from northern Illinois. Figure 1 is a composite of the observed moist room expansions giving an envelope within which all values have fallen. All 51 specimens are at least one year old and some are as old as 5 years. From present trends, it is highly unlikely that any specimens will fall outside the dashed lines shown for the older ages. These bars were made in all cases using cements with alkali contents, expressed as Na_2O equivalent, between 0.67 and 0.85 percent. In nearly all cases, the cement consisted of a blend in equal amounts of three brands. As expected, the observed expansions are small and exhibit no tendencies typical of the alkali-carbonate reaction.

Figure 2 shows similar data for 19 limestone samples. The quarries from which these originated, range from northern Ohio and Illinois to northern Michigan. Extrapolation of the data out to 4 years age was made similarly to that of the gravels and appears entirely justified by the data presently available. In this case, all specimens were made with cements having alkali contents ranging from 0.67 to 0.82 percent. These particular limestones exhibit expansions only slightly greater than that of the gravels. This behavior contrasts with that of three other limestones, data on which are shown later.

was stabilized in tap water and each cylinder was then immersed in NaOH solution in a separate polyethylene container.

Length measurements were made weekly using a dial comparator calibrated to 0.0001 in. At the end of 1 yr, tests on many specimens showing no expansion were discontinued and length measurements on the remaining samples were made at longer intervals. The expansive samples are still under test.

Water absorption determinations were made on all specimens, but the data are too numerous to be included in this paper.

Figure 1. Deteriorated concrete with Gull River carbonate rock as coarse aggregate.

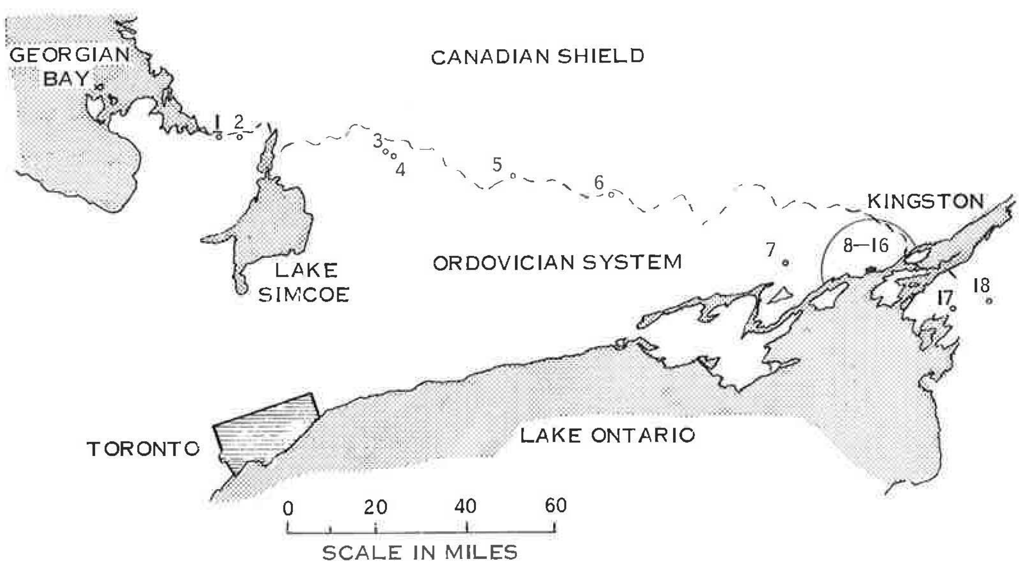

Figure 2. Locations of sampled Gull River rocks.

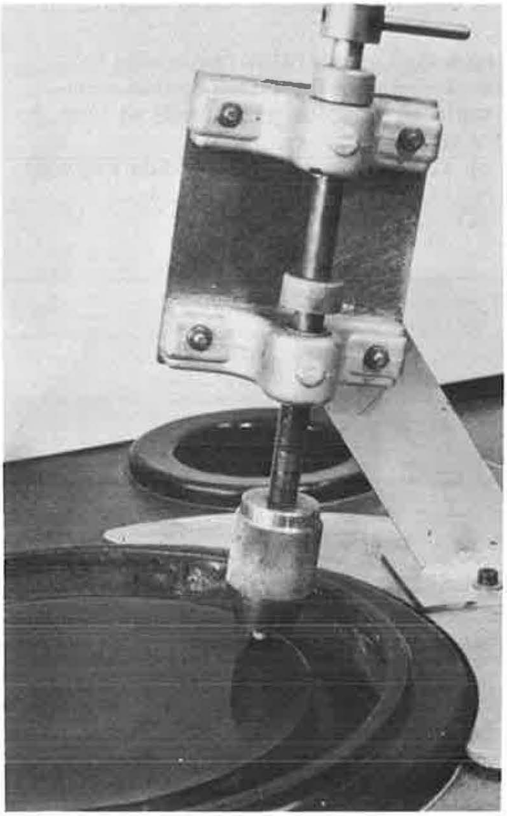

Figure 3. Jig and grinding lap for cutting cylinders conically to required length.

Petrographic Examinations

Because several petrographic features are reported to be significant for carbonate rocks showing expansion in concrete, material adjacent to the locations in the samples from which the test cylinders were taken was examined. All specimens were examined in thin sections for determination of texture and general composition. The percentage of noncarbonate impurities was determined using a 20 percent HCl solution at a maximum temperature of 60 C. Cursory determination of the type of carbonate rock (limestone or dolomite) was made by means of the copper nitrate staining test (2).

On the expanding samples only, partial chemical analysis was carried out to establish the calcite to dolomite ratio, and quantitative X-ray analysis of the acid insoluble material was conducted by R. Laakso of the Ontario Department of Mines to establish the type and approximate amount of noncarbonate impurities; i. e., the clay minerals and the main clastic minerals. X-ray diffractometry was also used to confirm the calcite to dolomite ratio calculated from chemical analyses.

RESULTS OF EXPANSION TESTS

Up to this time, a total of 170 cylinders (including four cylinders that showed definite expansion but broke after 4 to 29 wk of immersion) representing 17 Gull River locations have been immersed in 1 N NaOH solution for periods of from 1 to 2 yr. After immersion in NaOH most of the cylinders showed changes in size and some showed cracking.

Sixty-one cylinders representing eight locations expanded more than 0.1 percent, considered to be the lower limit of significant expansion. Of the comparison samples only five cylinders from the gravel particles were of the expansive type and are included in the following discussion on expanding Gull River carbonate rocks.

Cracking of the cylinders immersed in NaOH indicated the presence of spots or zones of weakness in the rock which would not necessarily cause cracking in concrete[1] where the rock is confined. The fact that highly cracked specimens (Fig. 13, Appendix) may not break indicates that the zones promoting cracking are normally very limited.

Amount of Expansion vs Duration of Exposure to NaOH

The 66 expanding cylinders may be divided into three groups based on the amount and time of maximum expansion observed:

1. Minor-expansion group[1]—expansion from 0.10 to 0.39 percent.
2. Early-major-expansion group—expansion of at least 0.40 percent, showing expansion in 2 to 5 wk. This group usually reached its maximum expansion in 10 to 40

[1] The lower limit allows an appropriate margin for testing error; the upper limit was selected arbitrarily.

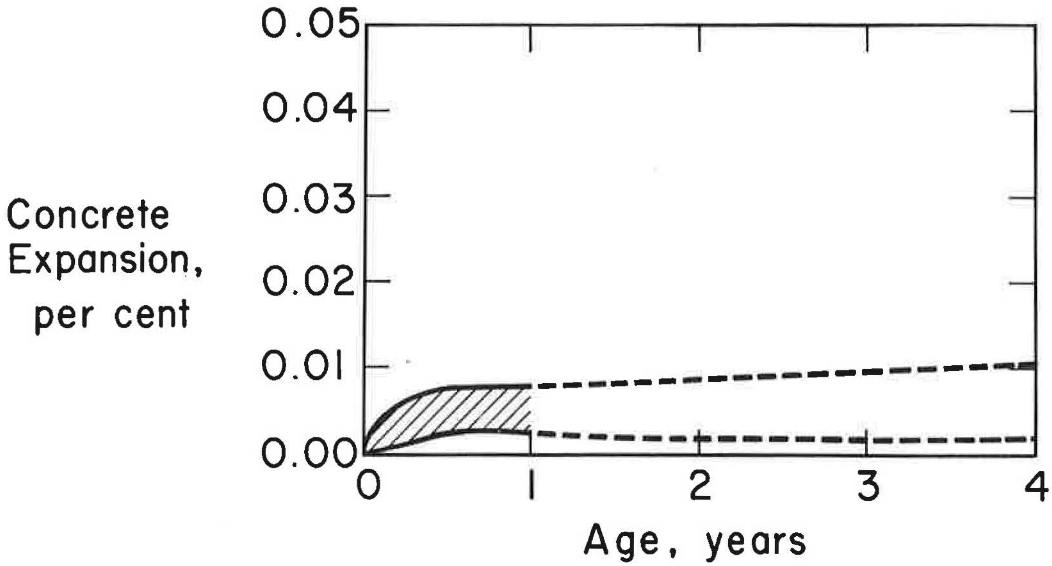

Figure 1. Envelope of expansions of moist stored concrete made with 17 different glacial gravels.

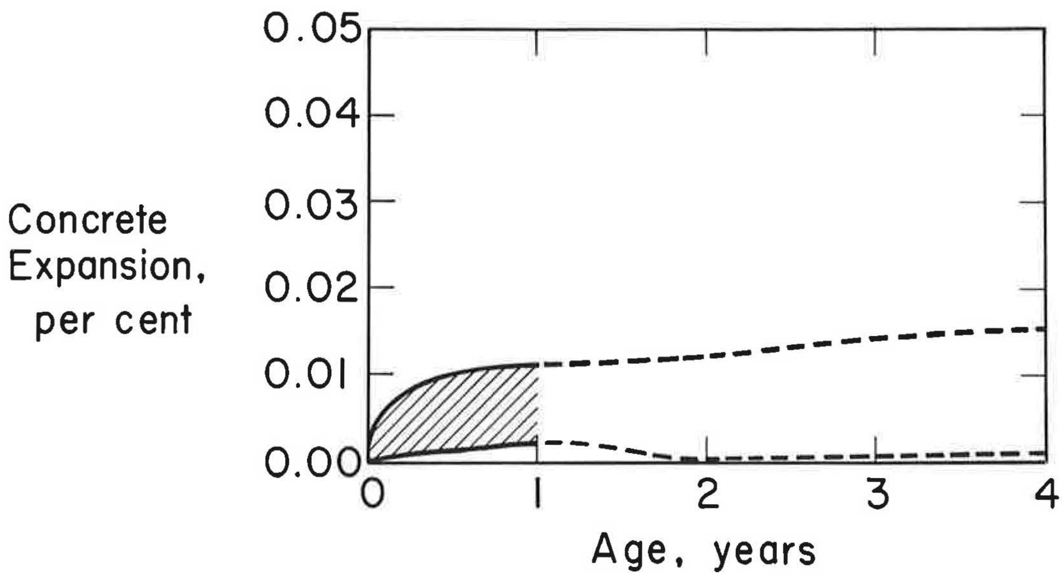

Figure 2. Envelope of expansions of moist stored concrete made with 19 different non-reactive limestone coarse aggregates.

TABLE 1

CONCRETE EXPANSIONS AND FREEZE-THAW DURABILITY RELATED TO CEMENT ALKALIES FOR LIMESTONES NO. 1 AND NO. 2

Series	Coarse Aggregate	Cement		Freeze-Thaw Durability Factor	Moist Storage Concrete Expansion, 4 yr (%)
		Designation	Alkali, Na_2O Equiv. (%)		
No. 1	Limestone no. 1	A	0.80±	32	0.036
	Gravel no. 1	A	0.80±	38	0.005
	Gravel no. 2	A	0.80±	8	0.007
No. 2	Limestone no. 1	B	0.21	63	0.013
	Limestone no. 1	C	0.68	20	0.031
	Limestone no. 1	D	0.85	29	0.043
No. 3	Limestone no. 1	E	0.26	80	0.010
	Limestone no. 2	E	0.26	80	0.007
	Gravel no. 5	E	0.26	13	0.004
	Limestone no. 1	F	0.60	41	0.023
	Limestone no. 2	F	0.60	65	0.012
	Gravel no. 5	F	0.60	13	0.009
	Limestone no. 1	G	0.87	19	0.038
	Limestone no. 2	G	0.87	32	0.017
	Gravel no. 5	G	0.87	12	0.008

Routine freeze-thaw testing of one limestone (identified as No. 1, hereafter) several years ago revealed two items: (a) the durability factor was considerably lower than expected, and (b) this was accompanied by appreciably greater expansions of the accompanying moist stored expansion bars. Two companion gravel samples tested simultaneously had the usual low expansions and poor to mediocre durability as would be predicted from the known content of deleterious particles. Unfortunately, the exact alkali content of the particular lot of cement from which these specimens were fabricated is unknown. However, this testing was performed with cement from a single source, and prior and subsequent tests of cement from this mill indicated the probability of about 0.8 percent alkali. These tests are identified as Series No. 1 in Table 1.

To verify that this limestone was sensitive to alkali content of the cement, Series No. 2 tests (Table 1) were conducted wherein three cements of determined alkali content were individually incorporated with limestone No. 1 in freeze-thaw specimens and expansion bars. These tests revealed a definite pattern of greater expansion with the high alkali cement accompanied by interior laboratory freeze-thaw durability. The durability factor of 20 with the intermediate alkali cement versus 29 with the highest alkali cement is not in strict order of decreasing durability with higher alkali cement. However, the substantially improved durability with the lowest alkali cement is unmistakable. At the time, it was not realized that the major expansion would take place within about the first 24 months for this limestone, and it seemed possible that very substantial expansions would ultimately occur. This has not proved to be the case.

To confirm better the pattern of behavior which was observed, a third series of tests was devised wherein cements of three alkali contents were individually incorporated in concrete containing each of three aggregates, one of which was limestone No. 1 which had shown tendencies for expansion in moist curing room storage. The second material selected for this series was a crushed limestone (No. 2) from a quarry which has been considered of borderline acceptability for many years. This stone typically breaks into slabby particles when crushed and requires fairly high sand contents in concrete to maintain workability with consequent high water demand. Sulfate soundness losses are typically high. Examination of pavements using limestone No. 2 as a coarse aggregate reveals rather frequent shale pop-outs but has not positively established poor service behavior, and the stone is widely used in its market area. The Department does not permit its use in exposed concrete in structures. The third aggregate selected for this series was a natural gravel (No. 5) which has been widely used without serious doubts as to its intrinsic durability but which has a chert and soft stone content contributing to numerous pop-outs. Heavy media treatment of this gravel has subsequently been successful in alleviating this problem.

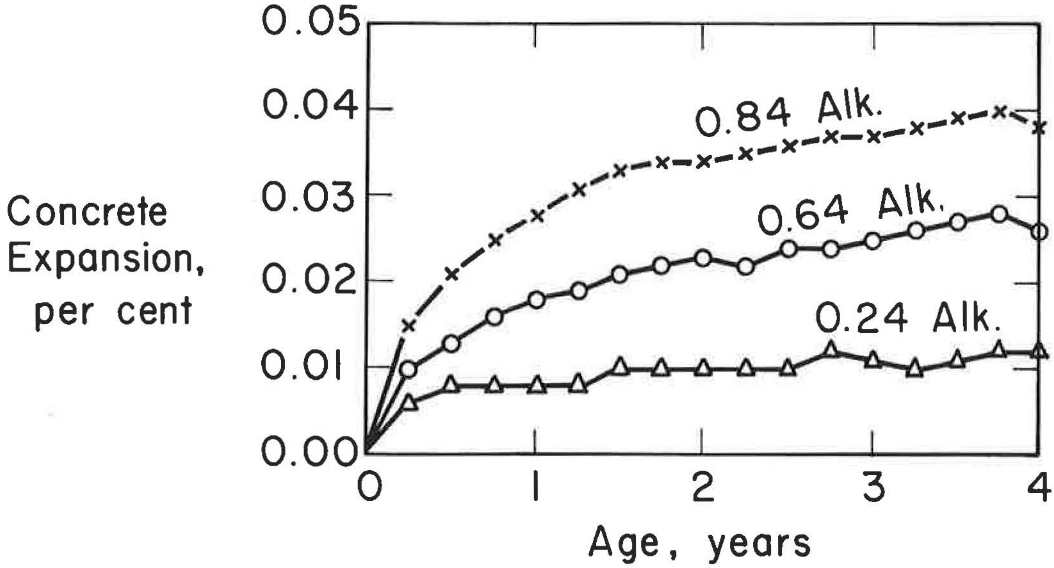

Figure 3. Effect of cement alkalies on expansion of concrete made with mildly reactive limestone no. 1.

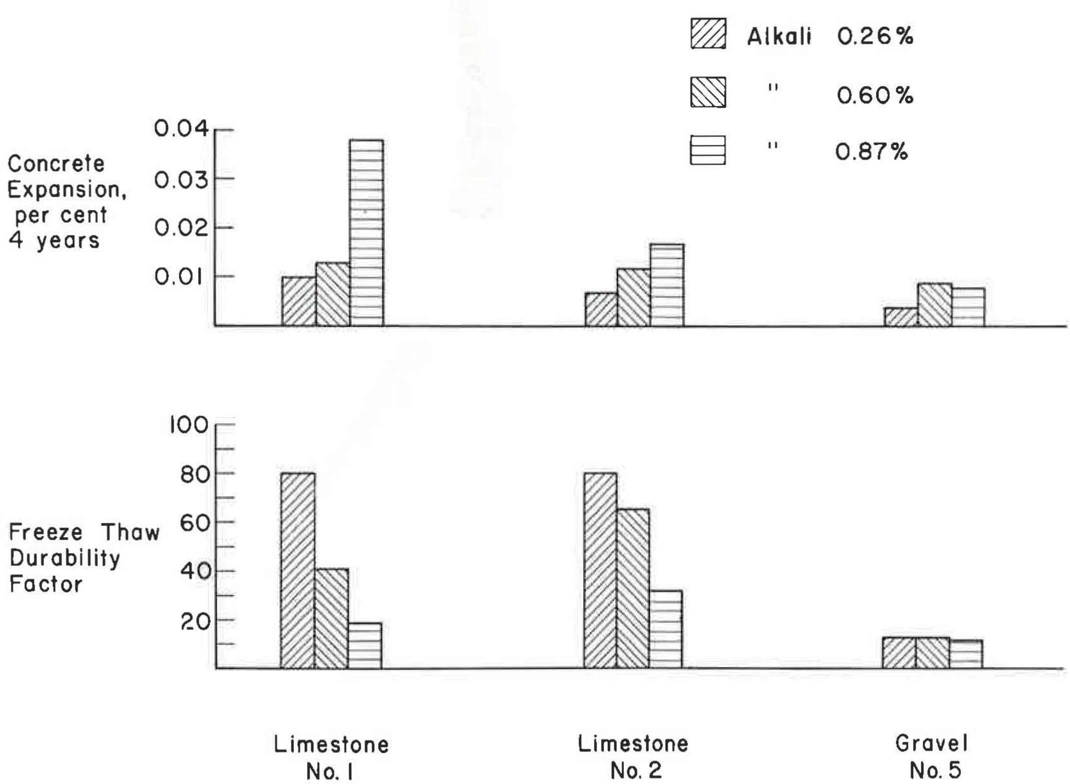

Figure 4. Series No. 3 tests of three coarse aggregates in concrete containing cements of three alkali contents.

TABLE 2

CHEMICAL ANALYSES OF CEMENTS USED IN SERIES 1, 2 AND 3 TESTS

Determination	Analysis (%)						
	A[1]	B	C	D	E	F	G
Silicon dioxide, SiO_2	20.4	20.5	20.9	20.7	21.0	21.2	21.3
Aluminum oxide, Al_2O_3	6.1	5.8	4.9	5.8	5.7	5.1	5.3
Ferric oxide, Fe_2O_3	2.8	2.2	2.9	3.1	2.4	2.6	2.7
Calcium oxide, CaO	64.3	62.5	63.0	62.3	63.0	63.4	64.1
Magnesium oxide, MgO	2.4	3.4	3.3	3.8	2.9	3.3	2.4
Sulfur trioxide, SO_3	2.5	2.3	2.3	1.9	2.3	2.4	2.1
Loss on ignition	1.2	2.7	1.5	1.2	1.8	1.3	0.9
Sodium oxide, Na_2O	0.21	0.14	0.21	0.27	0.15	0.20	0.40
Potassium oxide, K_2O	0.90	0.11	0.72	0.88	0.16	0.61	0.72
Insoluble residue	0.24	0.31	0.09	0.14	0.11	0.12	0.10
Total alkali, Na_2O equiv.	0.80	0.21	0.68	0.85	0.26	0.60	0.87
Calculated compounds:							
C_3S	55	50	54	47	49	52	54
C_2S	17	21	19	24	24	22	21
C_3A	11	12	8	10	11	9	9
C_4AF	9	7	9	9	7	8	8

[1] Chemical analysis of cement from mill at about the time Series No. 1 specimens were made (Table 1).

TABLE 3

CHARACTERISTICS OF LIMESTONES

Limestone No.	Sp. Gr. Bulk Dry	Absorption (%)	Dolomite/Total Carbonate Ratio	Insoluble Residue (%)
1	2.65 - 2.67	0.94 - 1.13	0.26	10.6
2	2.62	1.22	0.05	21.4
3	2.71	1.04	0.57	7.7
4	2.65	0.63	0.06	1.2
5	2.63	2.06	0.96	4.5
6	2.72	1.30	0.95	4.9
7	2.60	2.37	0.96	—
8	2.62	1.83	—	—
9	2.63	1.92	—	—
10	2.45	2.67	—	—
11	2.53	2.37	—	—
12	2.76	0.53	0.98	0.7
13	2.62	1.64	0.97	0.5
14	2.58	1.15	—	—
15	2.31	4.63	—	0.7
16	2.59	1.31	—	0.4
17	2.60	1.07	—	2.9
18	2.63	0.89	—	3.4
19	2.57	1.92	—	2.0
20	2.54	2.51	—	2.7
21	2.64	0.84	—	3.8
22	2.62	1.84	0.95	—

In conducting the Series No. 3 tests every effort was made to provide strictly comparable specimens by rotating the making of the nine combinations of materials (27 batches). All specimens were placed side-by-side in the moist room and scheduled into freeze-thaw in strict rotation to compensate for time-dependent variations. Because there were 81 beams involved that exceeded the capacity of the freeze-thaw equipment, making of test batches was delayed until there was assurance that the beams could be accommodated in the freeze-thaw chamber.

Expansion curves for concrete containing limestone No. 1 and using cement with three levels of alkali content are shown in Figure 3, up to an age of four years. The curve for the higher alkali cement is an average of values obtained in Series 1, 2 and 3. The curves for moderate and low alkali cements are averages of results from Series 2 and 3.

The results of the No. 3 series of tests are given in Table 1 and shown in Figure 4. Limestone No. 1 again shows larger concrete expansions accompanying its use with higher alkali cement as was indicated in the Series No. 2 tests. Conversely, the freeze-thaw durability factor diminishes with increased cement alkalies. Limestone No. 2 shows similar responses to cement alkalies but to a lesser degree. The gravel appears to be entirely insensitive to cement alkalies both as to expansion and freeze-thaw durability. Chemical analyses of the cements used in these tests are given in Table 2.

Limestone No. 3 from another quarry in the same general geological formation as limestone No. 1 was tested later and has shown 0.02 percent expansion at 2 years. This limestone was tested with a moderately high alkali cement, 0.82 percent, but had a relatively high durability factor of 86.

Evidence is not conclusive that other limestones, not showing expansion in moist room storage, would likewise display durability related to alkali content of the cement. However, several of the limestones incorporated with moderately high alkali cement and whose low expansions are reported in Figure 2 had high durability factors (in the 80's or 90's), and it seems unlikely that use of low alkali cement would show much improvement in durability.

The second line of evidence showing that the unusual freeze-thaw behavior of these limestones may be related to their expansions in moist room storage is somewhat more tenuous. This relates to their chemical composition which confirms, to a degree, the observations of Hadley (3). Table 3 lists the dolomite-total carbonate ratio and insoluble residue determinations, where available, for the limestones reported in this study. Dolomite was determined by wet chemical analysis on the assumption that all the magnesium carbonate occurred as dolomite (54 percent calcium carbonate and 46 percent magnesium carbonate) and the remainder of the calcium carbonate as calcite. Insoluble residue was determined using 3N hydrochloric acid as suggested by Lemish et al. (4). Limestones Nos. 1 and 3 have shown concrete expansions in moist storage and approach the intermediate dolomite content, with simultaneous appreciable insoluble content, which Hadley found to be significant criteria for distinguishing alkali-sensitive limestones. Limestone No. 2, although having a low dolomite content, has a high insoluble content which may explain its expansion behavior.

SUMMARY

1. Michigan's experience to date with alkali-carbonate rock is largely negative. Only three limestones have been found displaying expansive characteristics when incorporated in concrete with high alkali cement and subjected to moist room storage, and none of these expansions is of such magnitude, even after 4 years, as to predict adverse field behavior. Stone from one of these quarries has been used for more than 40 years as concrete coarse aggregate but is acknowledged to be the subject of controversy as to satisfactory service record. The present study would predict better performance if used with low alkali cement. None of the gravels studied shows significant expansions under similar exposure.

2. Two of the three limestones showing mild moist room expansions display much improved freeze-thaw resistance, when vacuum saturated in concrete, if used with a low alkali cement. The third limestone (No. 3) has not yet been studied in this regard but in view of its good durability with a high alkali cement, no appreciable improvement would be expected. The authors postulate that for limestone No. 1, dedolomitization in the freeze-thaw beams during the 14-day submerged curing period opens up the internal rock structure allowing greater water penetration and thus greater vulnerability to frost attack. In the case of limestone No. 2, inasmuch as the dolomite content is so low, it seems more likely that the large insoluble content is playing the dominant role.

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