LATE-EXPANSION ALKALI-REACTIVE CARBONATE ROCKS

Ludmila Dolar-Mantuani, Structural Research Department, Ontario Hydro, Toronto

Some alkali-reactive carbonate rocks of the Ordovician Gull River formation in Ontario are characterized by a shrinkage period preceding expansion when tested in 1N sodium hydroxide. These late-expansion rocks have a shrinkage period of at least 10 weeks, maximum shrinkage of at least 0.03 percent, and later minimum expansion of 0.20 percent. Petrographic examinations show the rocks to be sandy or silty argillaceous calcitic dolomites. Typical samples have 3 to 5 percent absorption, bulk specific gravity below 2.60, more than 20 percent acid-insoluble residues, and 75 to 87 percent dolomite in the carbonates.

•THIS PAPER reports on the continuation of the studies of carbonate rocks from the Ordovician Gull River formation, an important source of concrete aggregate, which outcrops in a narrow band along the southeastern border of the Canadian Shield in Ontario. Some Gull River rocks react with the alkalies in concrete and with alkali hydroxide solutions. Previous results of tests on these rocks in 1N sodium hydroxide were reported in 1964 (1). Many of the initial rock cylinders have now been tested for up to 8 years, and new samples have been added.

Many carbonate rocks shrink in alkali solutions before they start to expand (2,3,16). Five cylinders from one quarry in the area examined previously showed late-expansion characteristics that were distinctly different from those of the more abundant early-expansion group. Of this late-expansion group, 38 cylinders from four locations have now been tested. The expansion and petrographic features were compared with 248 other expansive and nonexpansive Gull River carbonate rocks. A few carbonate rocks from other Paleozoic formations were tested for comparison.

EXAMINATION METHODS

Expansion measurements on the rock cylinders essentially followed ASTM Designation C 586-69. Small pieces for petrographic studies were taken from the rock next to each cylinder. Thin-section analyses and acid-insoluble residue determinations using 20 percent hydrochloric acid were made on all samples. From 282 samples tested, the non-carbonate fractions of 84 were studied using X-ray diffraction by R. Laakso of the Ontario Department of Mines. Calcite and dolomite percentages were calculated for 98 samples, assuming that all of the MgO was present in dolomite. Magnesium and calcium were determined by wet chemical methods and by atomic absorption spectrophotometry. Calcite and dolomite percentages were also determined on -200 mesh material in 35 samples using evolution displacement (5) by W.O. Taylor of the Department of Mines. Differences in the calcite-to-dolomite ratio by the three methods were small. Information on porosity changes that occurred during NaOH exposure was obtained by absorption and specific gravity tests. These were made at atmospheric pressure and at 15 mm Hg (4) on small pieces of each late-expansion sample and at normal pressure on undamaged cylinders after 5 to 7 years of testing.

DISTINCTIVE CHARACTERISTICS

With the additional data obtained, a better definition of the late-expansion group can be made. The other groups have been redefined to conform with published data. In this

paper, carbonate rocks are defined as late-expansion if they meet the following conditions: (a) the initial shrinkage lasts at least 10 weeks, (b) the maximum shrinkage is at least 0.03 percent, and (c) the later expansion is at least 0.20 percent. The 0.20 percent expansion limit is from Sherwood and Newlon $(\underline{6}$, compare $\underline{17}$), but their time of 26 weeks for expansion was not adopted. A few carbonate rocks that shrank for less than 10 weeks or had minimal shrinkage were added to groups 1 or 2 listed in the following.

The few carbonate rocks were divided into four groups:

- 1. Early-expansion rocks (82 cylinders tested) with a maximum expansion of over 0.20 percent.
- 2. Rocks (35 cylinders) with insignificant expansion, up to 0.10 to 0.20 percent. These are part of the minor-expansion group defined in 1964 (1) as having maximum expansion of 0.10 to 0.38 percent. Cylinders expanding above $0.\overline{20}$ percent are now included in group 1. A lower limit of 0.10 percent was used by Buck (7).
 - 3. Nonexpansive rocks (125 cylinders) with a maximum expansion below 0.10 percent.
- 4. Shrinking carbonate rocks (35 cylinders) with only negative values for length changes.

RESULTS OF TESTS

Out of 282 samples (315 cylinders) of the Gull River carbonate rocks from 22 locations, 34 are represented by 38 cylinders and belong to the late-expansion group. Thirty were taken from two quarries at one specific level in each quarry. Because this group was not recognized at first, tests of cylinders that did not expand were stopped after 52 or 70 weeks, and the rocks were classed as nonexpansive (1). Some may have been late-expanders, but retesting of a few after a lengthy dry period failed to show late-expansion characteristics.

Expansion Characteristics

Shrinkage measured shortly after immersion in NaOH followed by long-term expansion, characteristic of the late-expansion group, is given in Table 1. Expansion may be gradual, up to 4 years, or sudden. The lengthy delay before expansion starts concealed the reactivity of rocks tested for too short a time. The shrinkage and expansion trends of this group are given in Table 2.

The shrinkage is significant, and growth beyond the original water-stablized length may not occur for over 2 years. However, some length increase occurs sooner because the maximum shrinkage is usually passed after 6 months of testing, and then the negative values start to decrease. No relationships were found among the parameters given in Table 2, except that shrinkage values over 0.20 percent were associated with longer shrinkage periods. Petrographic characteristics help in recognition of the type.

The expansion characteristics of the late-expansion group are evident in comparison with the early-expansion group shown in Figure 1. The number of samples decreases with time because cylinders are withdrawn. The early-expansion cylinders usually expand in the first 6 months of alkali immersion and then length changes become smaller, but the late-expansion group may not start to expand in 6 months. This feature should make early distinction between the two groups possible, even though at later stages the confidence envelopes and means overlap. This is not critical, however, because the objective is to find early signs of potential alkali reactivity.

Whether a rock belongs to the late-expansion group or to one of the nonexpansive of slightly expansive groups cannot be decided early. The enlarged insert in Figure 1 shows this. The very narrow (up to ± 0.02 percent) 95 percent confidence envelopes of the three nonexpansive groups are omitted, but that of the early-expansion group, which widens early and later is about the same as at the end of the first half year, is shown in the main graph.

Early recognition of the late-expansion group as being alkali-reactive is important. The difficulty in obtaining reliable results on expanding carbonate rocks at 2 and 5 weeks testing has been pointed out (Fig. 6 of $\underline{1}$). Late-expansion rocks are hard to identify

TABLE 1 LATE-EXPANSION CARBONATE ROCKS

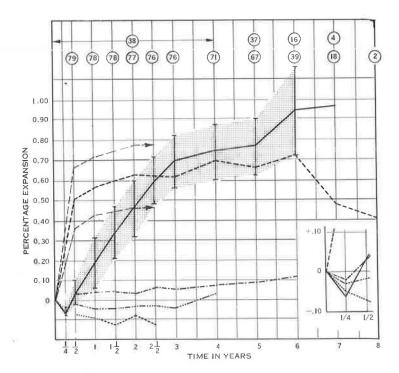
| | Petrographic Data | | | Summary of Length Change Based on Yearly Values in Percent | | | | | | | | | |
|----------------|---|-------------------------------|--|--|------------------|--------|--------|-------|-------|-------|-------|-------|----------------------------|
| Cylin- der | Insoluble Residue (weight percent) | Calcite/ Dolomite Ratio | Absorp- tion (weight percent) | Immersion Time in NaOH in Years | | | | | | | | | Crack- ing ^a |
| | | | | 1/4 | 1/2 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| 20 | 29.2 | 0.15 | 4.69 | -0.142 | -0.041 | 0.332 | 0.896 | 0.970 | 1.045 | 1.087 | 1.004 | | |
| 21 | 25.9 | 0.22 | 4.66 | -0.133 | -0.099 | 0.390 | 1.078 | 1.095 | 1.128 | 1.170 | 1.103 | | |
| 22 | 26.0 | 0.27 | 3.17 | -0.074 | -0.041 | -0.042 | 0.788 | 0.987 | 1.144 | 1.235 | 1.211 | | |
| 26B | 21.1 | 0.30 | | -0.075 | 0.125 | 0.150 | 0.250 | 0.308 | | | | | |
| 112A | 2.8 | 1.15 | 0.22 | -0.025 | -0.008 | 0.017 | 0.187 | 0.238 | 0.357 | 0.374 | 0.332 | 0.340 | Crack |
| 125A) | | | Y | -0.066 | -0.116 | -0.149 | 0.098 | 0.280 | 0.506 | 0.589 | | | |
| 125B) | 34.4 | 0.32 | 3.19 | -0.053 | -0.080 | -0.134 | -0.098 | 0.089 | 0.436 | 0.436 | 0.532 | 0.548 | |
| 126A) | | | | -0.016 | 0.141 | 0.656 | 0.856 | 0.856 | 0.914 | 0.955 | 2 | | |
| 126B | 25.9 | 0.19 | 4.30} | -0.116 | -0.099 | 0.357 | 0.839 | 0.922 | 0.972 | 0.956 | 0.764 | 0.764 | Crack |
| 127A) | | | · · · · · · · · | -0.041 | -0.107 | -0.158 | 1.261 | 1.966 | 2.356 | 2.348 | | | |
| 127B) | 48.5 | 0.20 | 3.57 | -0.008 | 0.076 | -0.051 | 0.358 | 0.417 | 0.604 | 0.613 | 2.165 | 2.174 | Crack |
| 181 | 30.1 | 0.22 | 4.55 | -0.058 | 0.199 | 0.625 | 0.641 | 0.716 | 0.616 | 0.683 | 0.691 | | |
| 182 | 31.7 | 0.25 | 4.87 | -0.049 | 0.174 | 0.574 | 0.599 | 0.690 | 0.640 | 0.632 | 0.632 | | |
| 183 | 35.2 | 0.19 | 5.20 | -0.041 | 0.083 | 0.258 | 1.047 | 1.164 | 1.064 | 1.089 | 1.072 | | Crack |
| 184 | 35.8 | 0.19 | 4.76 | 0 | 0.033 | 0.349 | 1.221 | 1.205 | 1.155 | 1.254 | 1.254 | | Crack |
| 185 | 34.4 | 0.27 | 4.76 | -0.016 | 0.348 | 0.581 | 0.573 | 0.698 | 0.540 | 0.615 | 0.615 | | Crack |
| | 34.4 | 0.27 | | 0.018 | | 0.663 | 0.688 | 0.829 | 0.780 | 0.771 | 0.771 | | |
| 186A) 186B) | | 0.25 | 5.32 | -0.074 | $0.165 \\ 0.149$ | 0.448 | 0.431 | 0.539 | 0.489 | 0.514 | 0.514 | | |
| 187 | 33.7 | 0.22 | 4.98 | 0.033 | 0.632 | 1.123 | 1.114 | 1.198 | 1.164 | 1.114 | 1.123 | | |
| 188 | 36.5 | 0.22 | 4.96 | 0.082 | 0.663 | 1.277 | 1.244 | 1.269 | 1.302 | 1.236 | 1.236 | | |
| 189 | 33.5 | 0.22 | 5.28 | -0.058 | 0.351 | 0.795 | 0.928 | 0.811 | 0.895 | 0.870 | | | |
| 195 | 8.2 | 0.40 | 1.52 | -0.058 | 0 | 0.058 | 0.116 | 0.141 | 0.224 | 0.208 | | | Crack |
| 196 | 5.9 | 0.37 | 1.21 | -0.033 | 0.033 | 0.058 | 0.091 | 0.075 | 0.158 | 0.141 | | | |
| 224 | 5.7 | 1.15 | 0.45 | -0.024 | 0.024 | 0.149 | 0.224 | 0.157 | 0.215 | 0.249 | | | |
| 234 | 43.4 | 0.30 | 3.12 | -0.016 | -0.049 | -0.041 | 0 | 0.448 | 0.431 | 0.414 | | | Crack |
| 235 | 29.4 | 0.27 | 5.20 | -0.033 | -0.083 | -0.107 | 0.226 | 0.810 | 0.861 | 0.844 | | | |
| 236 | 26.9 | 0.33 | 4.35 | -0.091 | -0.108 | -0.083 | 0.165 | 0.645 | 0.628 | 0.612 | | | |
| 237 | 28.9 | 0.25 | 4.96 | -0.150 | -0.197 | -0.173 | 0.107 | 0.479 | 0.578 | 0.570 | | | |
| 238 | 35.5 | 0.19 | 3.40 | -0.074 | -0.074 | -0.058 | -0.091 | 0.232 | 0.215 | 0.232 | | | |
| 239 | 27.0 | 0.33 | 3.45 | -0.091 | -0.140 | -0.108 | 0.091 | 0.563 | 0.505 | 0.497 | | | |
| 240 | 24.8 | 0.33 | 4.20 | -0.132 | -0.198 | -0.223 | 0.099 | 0.637 | 0.538 | 0.538 | | | |
| 241 | 21.3 | 0.25 | 3.87 | -0.100 | -0.058 | 0.116 | 0.463 | 0.810 | 0.810 | 0.802 | | | |
| 242 | 28.2 | 0.23 | 4.32 | 0 | -0.035 | -0.035 | 0.261 | 0.732 | 0.819 | 0.828 | | | |
| 243 | 29.9 | 0.28 | 4.42 | -0.083 | -0.041 | -0.091 | 0.298 | 0.967 | 1.108 | 1.100 | | | Crack |
| 244 | 29.3 | 0.25 | 4.70 | -0.093 | -0.126 | -0.212 | 0.059 | 1.007 | 1.083 | 1.075 | | | Crack |
| 245 | 24.9 | 0.37 | 3.59 | -0.036 | -0.093 | -0.009 | 0.188 | 0.599 | 0.527 | 0.527 | | | J. HOM |
| 246 | 24.9 | 0.30 | 2.94 | -0.034 | -0.051 | 0 | 0.111 | 0.256 | 0.342 | 0.324 | | | |
| 247 | 25.8 | 0.35 | 3.33 | -0.157 | -0.132 | -0.174 | 0.041 | 0.423 | 0.497 | 0.489 | | | |

^aCracking after length change test.

TABLE 2
LENGTH CHANGE PARAMETERS OF LATE-EXPANSION GROUP

| Parameter | Mean | | ent Con- e Limit | Observed Range | | |
|--|-------|-------|---------------------|-------------------|--|--|
| | | Lower | Upper | | | |
| Maximum shrinkage, percent Time of maximum shrinkage, | -0.13 | -0.15 | -0.11 | -0.03 to -0.25 | | |
| weeks Time of first length increase | 24 | 17 | 30 | 2 to 81 | | |
| from original length, weeks | 48 | 38 | 58 | 11 to 119 | | |
| Maximum expansion, percent Time of maximum expansion, | 0.81 | 0.67 | 0.95 | 0.24 to 2.36 | | |
| weeks | 194 | 182 | 207 | 93 to 278 | | |

Note: Data are based on maximal values.



when tested at 12 or 26 weeks $(\underline{6},\underline{7})$. Figure $\underline{2}$ shows the expansion after 12 and 26 weeks related to expansion after 1 year. The 12-week graph shows that none of the late-expansion cylinders expanded 0.10 percent, which is the basis for classifying rocks as suspected of being alkali-reactive, and that 23 of the 82 early-expansion cylinders might not have been recognized. The 26-week graph shows that about one-fourth (10) of the late-expansion cylinders went from shrinkage to expansion and that most of the early-expansion cylinders were expanding, with 50 of them expanding more than 0.20 percent. The points in the lower left corners of the graphs represent cylinders that were still shrinking after 1 year of immersion in NaOH.

In the 12-week graph, the plots of the late-expansion group are scattered in the shrinkage area; in the 26-week graph they begin to align in the same direction as the early-expansion group. The best-fit regression line, for the early-expansion group only, is similar in both graphs. A comparison of the data in both graphs by student's t-test shows that there is no significant difference in time between the means of the early-expansion group at the 95 percent confidence level. The 12-week results are apparently satisfactory for recognition of the early-expansion group. But significant expansion at a later stage is often not seen until after 6 months of testing.

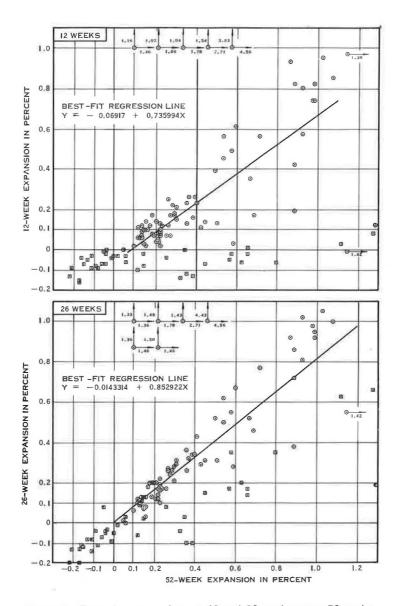


Figure 2. Expansion comparison at 12 and 26 weeks versus 52 weeks. Square denotes late-expansion cylinder; circle, early-expansion cylinder; solid line shows best-fit regression line for early-expansion cylinders only.

Influence of Cylinder Size on Expansion

Three cylinders, 145 mm in length and 50 mm in diameter, comparable in size to the prisms used by Swenson and Gillott (14), were drilled from two adjacent and parallel areas in a late-expansion layer and one from an early-expansion layer in the same quarry. Sets of four normal small-sized cylinders were drilled alongside of each of the large cylinders to compare the expansions with the expansions of the corresponding large cylinders. Figure 3 shows that the expansion of adjacent cylinders and the means of the adjacent sets were similar, but that the expansions of the large and the small cylinders were different. Small late-expansion cylinders had 22- and 15-week shrinking periods,

whereas large cylinders had only 8and 9-week delays in expansion. The examples show the great variability in results obtained by the sodium hydroxide immersion method.

Damage During Testing

Cracks were observed on 9 out of 38 late-expansion cylinders. cracks did not correlate with the amount or time of expansion or shrinkage, absorption characteristics, or amounts of acid-insoluble residue (Table 1). The usually shallow cracks occurred mostly in the central area of the cylinders. They could be wavy, branching, offset, or repeated at two (rarely three) levels. Only one cylinder (maximum expansion 1.35 percent) with one deep crack was bent. One cylinder had a fine network of hair cracks in a sandy portion, and another had a hair crack along three limonite concentrations, demonstrating the influence of compositional and textural weakness points.

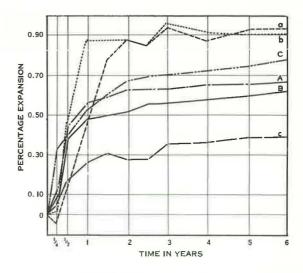


Figure 3. Comparison of expansion versus time of three large cylinders (A,B,C) and means of small cylinders (a, b.c) drilled from rock along side the large cylinders.

Unlike the early-expansion group, of which five cylinders broke early and many were cracked at the end of testing, none of the late expansion cylinders broke, which indicates greater resistance to alkalies. This is probably due to the greater porosity or slower rate of volume changes or both during the early stages of testing.

Indentations due to leaching were visible in small areas of a few cylinders (Fig. 4). The increase in absorption after testing shows that leaching occurred during NaOH immersion. The rocks are bleached after testing because of the loss of organic matter. The originally medium light gray (N6) of Munsell (11), rarely light gray (N7) grading to greenish gray (5GY6/1), became light to very light gray (N8) with slight greenish or more grayish hues in the aphanitic areas. Some cylinders contain spots of limonite from pyrite.

PETROGRAPHIC CHARACTERISTICS

sample were considered: specific gravities, absorption, acid-insoluble residue, calcite-

To characterize the late-expansion group, the following petrographic features of each to-dolomite ratio, noncarbonate minerals, texture, and petrographic classification.

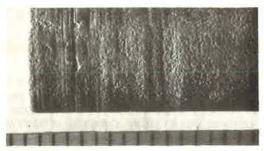


Figure 4. Etching marks on cylinder 169 tested for 5 years (scales in millimeters).

Physical Properties

The specific gravities and absorption determined at atmospheric pressure on single pieces of samples before testing and on undamaged cylinders after testing are given in Table 3. Absorption and specific gravities of a few undamaged earlyexpansive cylinders and several nonexpansive or slightly expansive cylinders were determined for comparison.

High absorption values and, for dolomites, relatively low bulk specific gravities are typical for the late-expansion

TABLE 3
SPECIFIC GRAVITIES AND ABSORPTION OF LATE-EXPANSION GROUP

| Characteristic | Mean | 95 Perce fidence | | Observed Range | |
|-----------------------------|--------------------------------------|---------------------|-------------|----------------|--|
| | | Lower | Upper | | |
| Atmospheric pressur | re, 24-hou | ır immers | ion in dis | tilled water | |
| Specific gravity, oven-dry | 2.50 | 2.47 | 2.54 | 2.41 to 2.59 | |
| Specific gravity, saturated | | | | | |
| surface-dry | 2.61 | 2.58 | 2.64 | 2.54 to 2.67 | |
| Specific gravity, apparent | 2.80 | 2.78 | 2.83 | 2.75 to 2.85 | |
| Absorption, weight percent | 4,27 | 3.99 | 4.55 | 2.94 to 5.32 | |
| 15 mm Hg vacuum, | 23 ³ / ₄ -hour | immersio | n in distil | led waterb | |
| Specific gravity, oven-dry | 2.51 | 2.47 | 2.54 | 2.42 to 2.59 | |
| Specific gravity, saturated | | | | | |
| surface-dry | 2.62 | 2.59 | 2.64 | 2.55 to 2.68 | |
| Specific gravity, apparent | 2.82 | 2.80 | 2.85 | 2.78 to 2.86 | |
| Absorption, weight percent | 4.52 | 4.21 | 4.83 | 3.08 to 5.65 | |
| Rock cylinders | after test | , atmosphe | eric press | urec | |
| Specific gravity, oven-dry | 2.28 | 2.24 | 2.33 | 2.14 to 2.55 | |
| Specific gravity, saturated | | | | | |
| surface-dry | 2.41 | 2.37 | 2.45 | 2.30 to 2.67 | |
| Specific gravity, apparent | 2.61 | 2.58 | 2.64 | 2.54 to 2.87 | |
| | | | | | |

^aWithout specific gravities of sample 234 (2,82 to 3,12), which contains celestite (true specific gravity 3,95 to 3,97).

rocks. This holds true for all typical samples regardless of their original locations within two quarries 140 miles apart. The 3 to 5 percent absorptions differentiate the late-expansion group from the early-expansion group $(\underline{6}, \underline{8})$. Such high absorption values and low bulk specific gravities usually indicate that the rock is physically unsuitable for use as concrete aggregate, but if no information is available on its reactivity it is usually tolerated if it occurs only in a few layers. Low bulk specific gravities and high absorption values are not always related to high maximum-expansion values $(\underline{10})$, but samples with less than 0.60 percent expansion have absorption below 3.6 percent.

The range in the difference between absorption under normal and low pressures is 0.04 to 0.57 percent, which is comparable with values found in fresh, vuggy, mediumgrained pure dolomites. This may indicate that these porous rocks contain some fine capillaries. There is no correlation between the absorption values and these differences in absorption.

The great increase in absorption of cylinders after testing 5 to 7 years (0.75 to 2.75 percent), in comparison with the absorption of the rock as received, indicates that significant leaching has taken place during immersion in NaOH; this effect has also been reported by others (9, 10, 18). The increase is greater in cylinders with expansions over 1 percent than in the others. Two cylinders showing only shrinkage had absorptions of 0.35 percent after $1\frac{1}{2}$ years of testing.

Texture and Composition

The principal constituent of late-expansion carbonate rocks is dolomite. Calcite, quartz, and clay minerals are major or minor constituents; feldspars, pyrite, limonite, and sulfates are accessory minerals. Single scales of mica and grains of tourmaline are visible in the thin sections.

The euhedral dolomite is 0.01 to 0.20 mm in grain size. The coarser rhombohedrons are finely dispersed in the finer grained mass (Fig. 5). The variation of grain size of dolomite suggests a second generation of a few larger sized dolomite grains. The small dolomite euhedra are clear, and clayey impurities in the larger grains are usually

b29 samples.

c25 undamaged cylinders, 4 to 7 years tested.

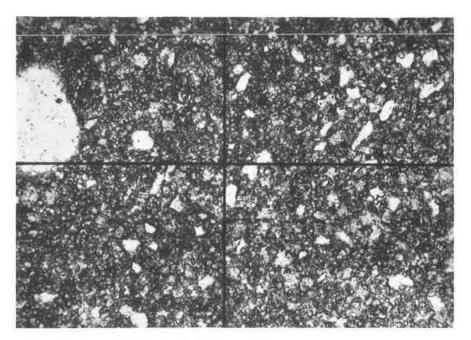


Figure 5. Large dolomite rhombohedrons and clear silt-sized detrital quartz seen in a matrix of very fine crystalline dolomite, calcite, and clay. Sand-sized grain is quartz (Sample 247; 88X).

scarce. Calcite occurs in the fine crystalline to aphanocrystalline (size less than 0.004 mm, 12) matrix together with dolomite and clay. Calcite may form larger patches of single grains typical of the poikilitic texture, with dolomite and rarely quartz as inclusions.

The rounded or angular silt to fine sand grains of quartz (0.01 to 0.10 mm) are scattered throughout the rock, concentrated in small areas (Fig. 6), or form a netlike structure. Small patches may give an impression of a dolomitic siltstone or sandstone. Quartz is always clear with uniform extinction. Fresh detrital feldspars of the same size as quartz occur in all samples in moderate or minor amounts. Potash feldspars are more abundant than plagioclases, the latter occurring as minor constituents or in traces. Most of the thin sections contain a few rounded quartz grains and, rarely single feldspar grains up to 1.0 mm in size.

Clay occurs in lenses, pockets, or interstices. The rare stylolites are usually very narrow concentrations of clay minerals and organic matter with a few detrital quartz grains. The clay minerals are represented mostly by illite and subordinately by chlorite. In three samples relatively rich in quartz, clay minerals are present in amounts not detectable by X-ray. Earlier X-ray examinations of five samples by Laakso indicated the presence of an expanding clay mineral in these samples. This is unlikely to be responsible for the expansive properties of the rock, however, because of the very small amounts involved (1).

Pyrite in single crystals or small concentrations may be partially altered to limonite; both minerals are ubiquitous. Sulfates are present in all samples, at least in traces. Five samples had more than 0.2 percent of sulfur trioxide in the filtrates from the acid-insoluble residues; one sample had 1.7 percent. Gypsum was not observed in the thin sections, but celestite was found in the 0.05- to 0.20-mm sizes of irregular grains as an accessory constituent.

The approximate amounts of quartz, illite, chlorite, potash feldspar, and plagioclases were established by Laakso by X-ray methods. There are variations in the

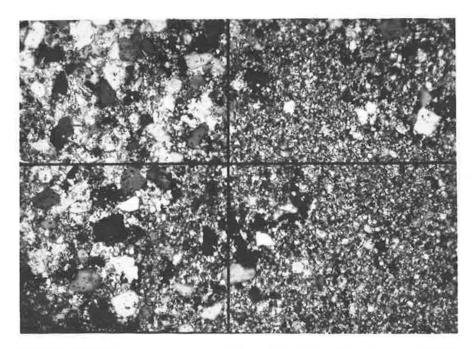


Figure 6. Very fine crystalline dolomite, calcite, and clay (right side) and accumulation of detrital silt-sized quartz (clear, uniform grains) and larger dolomite rhombohedrons in a very finely grained matrix (left side) (Sample 184; crossed nichols, 88X).

amounts of the constituents, some seemingly influenced by the source location of the samples. For example, rocks from one of the main quarries were poorer in clay minerals and contained very little chlorite and only traces of sulfates, whereas rocks from the other quarry always contained chlorite and sulfates usually in weighable amounts. One general difference between the late- and early-expansion rocks is the significant presence of quartz in the former. In agreement with the massive structure of the beds containing late-expansion rocks, bedding is usually not easily discernible in the samples.

On the basis of the calcite-to-dolomite ratio and the noncarbonate constituents, the rocks are classified as sandy or silty argillaceous calcitic dolomites. They are similar to the 24- to 30-ft bed in a Kingston quarry described in detail by Gillott (13).

Graphic Presentation

To obtain better characterization of the composition of the late-expansion rocks, the quantities of dolomite, calcite, and noncarbonates (acid-insoluble residue) have been plotted. This simplified composition is presented in a triangular plot like those used by Sherwood and Newlon ($\underline{6}$), with corners representing 100 percent of calcite, dolomite, and acid-insoluble residue plus SO $_3$ calculated as gypsum (Fig. 7). Plots of the early-expansion rocks and a few nonexpansive or slightly expansive rocks are included in Figure 7.

The late-expansion group is concentrated in a small area along the low calcite side, indicating little variation in the composition of the group. Determinations of the three components of 97 Gull River samples show that only two early-expansion and two nonexpansive rocks are located in this area. The early-expansion rocks are widely scattered in the lower portion of the triangle and are concentrated at the calcitic corner. The few plots of suspected expansive (x) and of shrinking (+) carbonate rocks are located in areas of expansive rocks. They meet the main compositional characteristics of expansive rocks but not the additional complex conditions for distinct alkali reactivity.

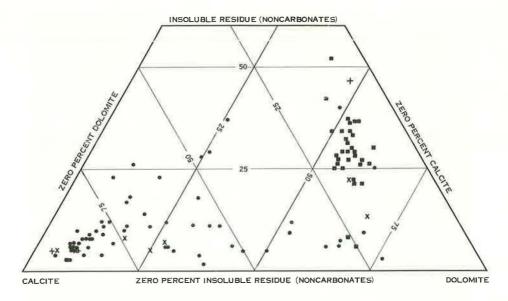


Figure 7. Ternary plot of composition of test samples. Solid square denotes late-expansion cylinder; solid circle, early-expansion cylinder; x, cylinder suspected of being expansive; +, nonexpansive cylinder.

RELATIONSHIP BETWEEN PETROGRAPHIC AND EXPANSION CHARACTERISTICS

Figures 8 and 9 show the compositional parameters related to the degrees of expansion. The amounts of acid-insoluble residue are between 21 and 49 percent. The upper limit of insoluble residue content is much higher for the megascopically uniform Gull River rocks than has been assumed $(\underline{1})$. Most of the rocks contain from 24 to 36 percent insolubles, whereas most of the early-expansion Gull River rocks contain less than 13

TABLE 4
CHARACTERISTICS OF BORDERLINE LATE-EXPANSION ROCKS

| Observator (all) | | Sam | Late-Expansion | | | |
|--|-------|-------|----------------|-------|--------|--|
| Characteristic | 112A | 195 | 196 | 224 | Groupb | |
| General properties | | | | | | |
| Maximum shrinkage, percent | -0.03 | -0.08 | -0.04 | -0.07 | -0.03 | |
| Time of maximum shrinkage, weeks | 22 | 9 | 15 | 9 | | |
| Duration of shrinkage, weeks | 41 | 22 | 23 | 20 | 10 | |
| Maximum expansion, percent | 0.41 | 0.24 | 0.26 | 0.29 | 0.20 | |
| Time of maximum expansion, weeks | 236 | 185 | 185 | 163 | _ | |
| Damage in NaOH | crack | crack | nil | nil | _ | |
| Petrographic properties | | | | | | |
| Bulk specific gravity | 2.70 | 2.71 | 2.73 | 2.69 | 2.50 | |
| Absorption at atmospheric pressure, | | | | | | |
| weight percent | 0.22 | 1.52 | 1.21 | 0.45 | 4.27 | |
| Absorption at 15 mm Hg, weight percent | 0.24 | 1.59 | 1.29 | 0.49 | 4.52 | |
| Acid-insoluble residue, weight percent | 2.8 | 8.2 | 5.9 | 5.7 | 31.5 | |
| Calcite/dolomite ratio | 1.15 | 0.40 | 0.37 | 1.15 | 0.27 | |

^aSample designations are as follows:112A, patchy (biopelmicritic) limestone; 195, medium crystalline dolomite (V:D4); 196, medium crystalline dolomite (V:D4); and 224, aphanitic limestone (d:III mX:L1).

blincluded for comparison; general properties given are minimum requirements for late-expansion group; petrographic properties given are mean values of typical late-expansion rocks (compare table 3).

percent; 25 cylinders with an expansion of more than 0.50 percent have acid-insoluble residues between 5 and 13 percent.

Figure 9 shows the restricted range for dolomite in the late-expansion group. These rocks have 75 to 87 percent dolomite in the carbonate constituents. They fall in the range of 70 to 90 percent dolomite that is reported to lack expanding representatives when rocks from Virginia were examined $(\underline{6})$. Few expansive carbonate rocks from the Gull River formation in Ontario have between $\underline{40}$ and 70 percent of the mineral dolomite $(\underline{14}, \underline{13}, \underline{8})$. There is no relationship between the amounts of expansion and the percentages of acid-insoluble residues and dolomite $(\underline{16})$.

Some Exceptions

Late-Expansion Rocks Not Having Essential Petrographic Features—Table 4 shows that four carbonate rocks are late-expanders by their expansion characteristics but not according to their petrographic properties (Fig. 7, 8, 9). The two dolomitic rocks occur in small areas in layers of early expansion rocks, and the two limestones occur in a quarry of apparently nonexpansive rocks.

Rocks Having Several Essential Petrographic Features But Not Classified as Late Expanders—Seventeen samples have residues over 20 percent typical of late-expansion rocks, but they are early-expansive, nonexpansive, or very slightly expansive. Chemical analyses showed that five are limestones and four do not meet the defined expansion requirement or were tested for too short a time. One dolomite from the contact between early- and late-expansion rocks contains only a few lenses typical of the latter group.

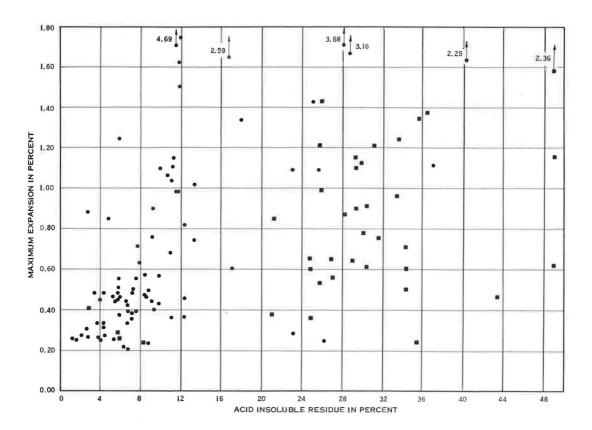


Figure 8. Acid-insoluble residue versus maximum expansion. Solid square denotes late-expansion cylinder; solid circle, early-expansion cylinder.

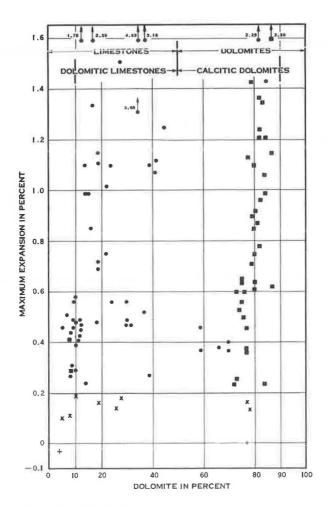


Figure 9. Dolomite in percent of carbonate portion versus maximum expansion. Solid square denotes late-expansion cylinder; solid circle, early-expansion cylinder; x, cylinder suspected of being expansive; +, nonexpansive cylinder.

The remaining seven samples do not conform to the late-expansion group on the basis of detailed thin-section examinations.

To establish minute microscopic differences or similarities, a comparison with thin sections of late-expansion rocks is essential. To establish that a rock belongs to the late-expansion group in principle may be possible, but it is impossible to predict how much it will expand, not even by means of the least-squares from petrographic parameters.

SUMMARY AND CONCLUSIONS

The late-expansion alkali-reactive carbonate rocks of the Gull River formation are well defined by their expansion and petrographic characteristics, but rocks from elsewhere may show variations. When immersed in 1N sodium hydroxide, this group is separated from the early-expansion group by a shrinkage of at least 0.03 percent for at least 10 weeks, during which the cylinders are shorter than the original water-stabilized length, and by a later expansion of a minimum of 0.20 percent. The maximum shrinkage period was more than 27 months.

Early recognition of the late-expansion group was not possible because no sample expanded enough to be classified suspect after 12 weeks of testing. Some may not expand after testing for 1 year. In contrast, the early-expansion rocks usually expand within 6 months. However, a sigmoidal curve representing the length changes of the late-expansion group, together with distinct petrographic features, should be helpful in detecting this type of rock after 6 months of testing.

The group is characterized by an absorption of up to 5 percent, with bulk specific gravity below 2.60, acid-insoluble residue from 21 to 49 percent, and a dolomite content of 75 to 87 percent carbonates. The high percentages of acid-insolubles indicate poor interlocking of carbonates and a low structural rigidity (10). The narrow range of the dolomite content is striking, but this may be because most of the late-expansion samples

came from one distinct level in two quarries.

Petrographically, the rocks are fine-grained sandy or silty argillaceous calcitic dolomites. The noncarbonate minerals include quartz and clay minerals—mostly illite and subordinately chlorite, potash feldspar, and plagioclase. Pyrite, limonite, sulfates, gypsum, and, in five samples, celestite are accessory constituents or are present in traces. Organic matter may be concentrated in rare stylolites. Detrital quartz is one of the major noncarbonate constituents. Other Gull River carbonate rocks with a high content of noncarbonates do not have much detrital quartz.

Four samples showed length changes in NaOH that were characteristic of the late-expansion group, but the samples also had some petrographic features typical of early-expansion rocks. Twelve samples had most of the petrographic features typical of the late-expansion rocks, but they did not have their expansion behavior. Such borderline cases reflect the normal complexity of rocks. The thorough study necessary for finding fine differences usually cannot be performed during normal examinations of rocks intended for use in concrete.

The expansive Gull River rocks were apparently sedimented under different environmental conditions. The late-expansion rocks were deposited under conditions of higher energy than the more abundant aphanitic dense early-expansion rocks $(\underline{15})$. The alkali

reactivity in both groups, however, is comparable.

Results obtained on different sizes of rock specimens may differ—a fact established for the carbonate rock aggregates in concrete (14). Standardization of size is strongly recommended for comparison of test results from different laboratories. Results on cylinders of two sizes illustrate the difficulties in determining acceptance limits. They further support the need for testing what are suspected to be alkali-reactive carbonate rocks in concrete before accepting them for use as concrete aggregates.

ACKNOWLEDGMENTS

The author thanks the Hydro-Electric Power Commission of Ontario for permission to publish this paper; D. Moddle, director of the Laboratory and Research branch of the Ontario Department of Mines for use of these facilities by R. Laakso and W. O. Taylor; A. L. Punhani of Ontario Hydro's Operations Research Group for statistical work; J. Engelhardt of the Chemical Research Department for chemical data; and R. B. Watts for processing most of the data on expansion, acid-insoluble residues, specific gravities, and absorption.

REFERENCES

- Dolar-Mantuani, L. Expansion of Gull River Carbonate Rocks in Sodium Hydroxide. Highway Research Record 45, 1964, pp. 178-195.
- 2. Axon, E. O., and Lind, Jr. Alkali-Carbonate Reactivity—An Academic or a Practical Problem. Highway Research Record 45, 1964, pp. 114-125.
- Lemish, J., and Moore, W. J. Carbonate Aggregate Reactions: Recent Studies and an Approach to the Problem. Highway Research Record 45, 1964, pp. 57-71.
- Dolar-Mantuani, L. Use of Petrography in Evaluation of Frost-Susceptible Natural Aggregate. RILEM Internat. Symposium on Durability of Concrete, Part 1, B-215-231, 1969.

- Dreimanis, A. Quantitative Gasometric Determination of Calcite and Dolomite by Using Chittick Apparatus. Jour. Sedimentary Petrology, Vol. 32, 1962, pp. 520-529.
- 6. Sherwood, W. C., and Newlon, H. H. Jr. A Survey for Reactive Carbonate Aggregates in Virginia. Highway Research Record 45, 1964, pp. 222-233.
- Buck, A. D. Potential Alkali Reactivity of Carbonate Rocks From Six Quarries.
 U.S. Army Engineer Waterways Experiment Station, Corps of Engineers, Vicksburg, Miss., Misc. Paper C-69-15, Oct. 1969, pp. 1-11.
- 8. Swenson, E. G., and Gillott, J. E. Alkali-Carbonate Rock Reaction. Highway Research Record 45, 1964, pp. 21-40.
- Feldman, R. F., and Sereda, P. J. Characteristics of Sorption and Expansion Isotherms of Reactive Limestone Aggregates. ACI Jour., Vol. 58, No. 2, Aug. 1961, pp. 203-214.
- Hilton, M. H. The Effects of Textural and External Restraints on the Expansion of Reactive Carbonate Aggregates. Virginia Highway Research Council, Prog. Rept. 7b, Sept. 1968, pp. 1-61.
- 11. Munsell's Rock-Colour Chart, 2nd Print. Geol. Soc. Amer., 1951.
- 12. Folk, R. L. Practical Petrographic Classification of Limestones. Amer. Assn. Petroleum Geologists, Bull., Vol. 43, 1959, pp. 1-38.
- 13. Gillott, J. E. Petrology of Dolomite Limestones, Kingston, Ontario, Canada. Geol. Soc. Amer., Bull., Vol. 74, No. 6, 1963, pp. 759-778.
- 14. Swenson, E. G., and Gillott, J. E. Characteristics of Kingston Carbonate Rock Reaction. HRB Bull. 275, 1960, pp. 18-31.
- 15. Gillott, J. E. Mechanism and Kinetics of Expansion in the Alkali-Carbonate Rock Reaction. Canadian Jour. of Earth Sciences, Vol. 1, No. 2, 1964, pp. 121-145.
- Missouri State Highway Department. Alkali Reactivity of Carbonate Rocks in Missouri. Missouri Cooperative Highway Research Program, Rept. 67-6, Aug. 1967, pp. 1-36.
- 17. Missouri State Highway Department. Effects of Reactive Carbonate Aggregates on the Durability of Laboratory Concrete Specimens. Missouri Cooperative Highway Research Program, Rept. 67-5, July 1967, pp. 1-46.
- 18. Walker, H. N. Alkali Carbonate Reaction Products Found in Mortar Bars and Prisms. Virginia Highway Research Council, Dec. 1967, pp. 1-35.