Part III. REGIONAL STUDIES

Expansion of Gull River Carbonate Rocks in Sodium Hydroxide

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The ALKALI-CARBONATE rock reaction that has caused serious deterioration of concrete (Fig. 1) appears to be limited in Ontario to rocks of the Gull River formation. This Middle Ordovician formation, which occurs in a narrow zone averaging about 10 mi wide along the southern border of the Canadian Shield, was formerly known as the Black River formation but was redefined by Liberty (6) on the basis of lithological characteristics.

Because many quarries (5), among them the classical Kingston quarries, are located in this formation, an investigation was conducted to establish whether the expansive type of rock found at Kingston occurs elsewhere in Ontario and, if so, whether it might be used by Ontario Hydro as concrete aggregate.

MATERIALS AND METHODS

Sampling

More than 200 samples were collected from 18 locations in the Gull River formation. The locations sampled in the 200-mi stretch from Georgian Bay to Kingston (Fig. 2) included eight operating quarries, four abandoned ones, and three highway cuts. The sampling extended to three locations of the Black River group (Adirondack Sheet, 1) south of the Canadian border. For comparison, a few carbonate rock samples from the overlying Bobcaygeon formation were included in the program, as well as 39 carbonate particles from two gravel pits outside the Gull River formation.

The samples were taken from the different megascopically distinguishable rock varieties occurring in the various locations. Most of the specimens used in this study were fresh and by normal evaluation techniques would be considered satisfactory for use as concrete aggregates.

Test Method

For convenience, the samples were tested for expansion in NaOH solution rather than in concrete. However, instead of large prisms (1 1/4 by 5 1/4 in.) as used by Swenson and Gillott (8), or small prisms (1/4 by 1 1/4 in.) as adopted by Hadley (4), small cylinders 3/8 in. in diameter and 1 1/4 in. in length were used. These cylinders were cut with a diamond drill from the rock samples at right angles to the sedimentation layers, if possible. The cylinders were cut to the required length and the ends were shaped conically by means of a jig and a normal grinding lap (Fig. 3); the length of the cylinders

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wk, after which the length of the cylinders either remained more or less constant or increased at a very slow rate.

3. Late-major-expansion group—expansion of at least 0.40 percent, starting to expand after 25 wk (in one case after more than 1 yr) and continuing to expand for the full testing period.

Rocks classified in the late-expansion group were found to be much less common than those classified in the minor- and early-expansion groups. Only five cylinders from two locations belonged to the late-expansion group, but these specimens were sufficiently well defined by expanding characteristics and petrographic characteristics to be considered separately as a distinct group. Furthermore, whereas layers may contain expanding rocks of both the minor- and early-expansion groups, it appears that those layers containing late-expansion rocks did not contain rocks of the other two expansion groups. On the other hand, minor- and early-expansion types occurred at the same locations as late-expansion rocks but in different layers.

The late-expansion group is probably one of the causes of the irregularly occurring and seemingly delayed expansion of concrete containing expanding carbonate rocks of the Kingston type.

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Figure 4. Expansion vs time for typical rock cylinders in NaOH immersion.
Figure 4 shows typical expansion curves of the three groups described, together with a curve characterizing the cylinders that did not expand. This graph shows the difference between the early-expansion group, which has a parabolic expansion curve, and the late-expansion group, which has a typical sigmoidal curve with negative values during the first 25 wk or more.

Many samples characterized by low expansion rates are found to have negative values at early testing ages. This phenomenon is typical for the late-major-expansion group, but shrinkage is developed most clearly in nonexpansive cylinders. The greatest decrease in length obtained in a Gull River rock was 0.26 percent for a nonexpansive cylinder having 46 percent of acid-insoluble residue. (The greatest reduction in length, 0.45 percent, was observed on a cylinder made of a Bobcaygeon rock that contained only 12 percent of noncarbonates.) The nature of these shrinkage phenomena is not known. Shrinkage could go undetected in cylinders having high early rates of expansion. If this phenomenon is a characteristic of slowly expanding cylinders only, then the expansion should be determined from the minimum length measured rather than from the length after water stabilization. However, because it could not be demonstrated that shrinkage did not occur in the early-major-expansion group, no corrections were made for the effect.

Figure 5 shows the individual curves of the major-expansion groups and a band representing the minor-expansion group. The testing of nonexpansive and some minor-expansion cylinders was terminated after 52 to 70 wk of immersion. The test results indicated that it is advisable, for full appraisal and understanding of a quarry, to continue the testing of all rocks by this method for at least 70 wk to be sure that all minor-expansion as well as late-major-expansion samples are detected.

The cylinder represented by curve 2 seems to belong to the minor-expansion group after 1 yr of testing. However, it has to be included in the late-major-expansion group because it was cut from the same rock specimen as the late-major-expansion cylinder, curve 1, and because it shows a typical expansion curve of that group. Both cylinders demonstrate the heterogeneous expansion behavior which might be encountered on small samples. An additional three samples that show more than usual differences in expansion between cylinder pairs taken from the same specimen are shown in the Appendix.

Expansion in Short-Duration Tests

The results of an attempt to predict the presence of expanding rocks in a location by their performance in NaOH solution in a relatively short-term test are shown in Figure 6, which contains the data for all expanding cylinders and for those nonexpansive cylinders which showed some expansion at the 2- and 5-wk periods but were classified as nonexpansive because they failed to reach 0.1 percent expansion during the whole testing period. The most important feature of this graph is that it shows that the late-expansion group would be completely overlooked in short-duration tests of 2 or 5 wk and might not even be recognized as a major-expansion group after 1 yr of testing.

From the limited tests carried out, it can be concluded tentatively that all cylinders showing more than 0.1 percent expansion in a 2-wk testing period belong to the early-major-expansion group, but one-third of the samples belonging to this group would not be recognized as such at the end of 2 wk. Furthermore, the graph shows that no information is available to indicate whether cylinders showing non-significant expansion (from 0.01 to 0.1 percent) at this time represent major-, minor-, or even nonexpansive rocks; one-half of the minor-expansion rocks would not show any length increase, thus behaving similarly to most of the nonexpansive rocks.

On the other hand, it appears that all cylinders showing a length increase above 0.1 percent after 5 wk of testing should be classified in the early-major-expansion group and cylinders showing a slight expansion (from 0.04 to 0.1 percent) at this time most probably belong to the minor-expansion group; but cylinders with a smaller expansion might be minor-expansion or nonexpansive rocks, because one-quarter of the 109 nonexpansive cylinders show a slight expansion (between 0.01 and 0.05 percent) not only at 2 but also at 5 wk. It is very difficult to establish by short-term tests which samples belong to the minor-expansion group, because of the variable-expansion behavior of this group at early test ages.
Figure 5. Expansion vs time for rock cylinders in NaOH; curves 1, 2, 3, 4 and 5 of late-major-expansion cylinders; other curves, early-major-expansion cylinders.
Figure 6. Expansion comparison in percent at two and five weeks vs 52 weeks: cross = nonexpansive cylinder, empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, and solid square = late-major-expansion cylinder.
Figure 7. Test duration vs maximum expansion: empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.
Maximum Expansion

The maximum expansion registered in the set tested for 1 to 2 yr was 3.5 percent. Figure 7 illustrates the great differences in the time taken for maximum expansion of various cylinders to occur. It also demonstrates the difference between the minor- and both major-expansion groups. When considering these data, however, it should be kept in mind that the tests are not yet completed and some cylinders will eventually show an even higher maximum length because the expansion may be continuing at a very slow rate. This applies especially to the samples that have been under test for only 1 yr.

PETROGRAPHIC CHARACTERISTICS OF EXPANDING GULL RIVER ROCKS

No single feature of composition or texture has been found to be connected with the expansion behavior of the Gull River rocks. Detailed examination of the expansive rocks showed certain megascopically noticeable heterogeneities such as differences in color, grain size, density, dolomite content, and presence of clay seams, quartz grains and fossils. This may apply not only to samples taken from different members of the same geological unit but also to different layers of the same geological member and even parts within a layer. On the other hand, rocks having a seemingly identical petrographic appearance might differ considerably in their expansion characteristics as shown in the Appendix by the differences in the responses of cylinder pairs to NaOH. These facts prevent prediction, on the basis of characteristics revealed by normal petrographic techniques, of whether a rock is expansive or not and to which expansion group it might belong.

Composition of Expanding Rocks

Percentage of Dolomite in Carbonate Portion.—The dolomite to calcite ratios of the rocks were determined in two ways, by X-ray analyses and by determining the calcium and magnesium contents by wet chemical analyses, and then calculating the ratio assuming that all of the magnesium was present as dolomite and the excess calcium was present as calcite. The results obtained by the two different methods do not differ significantly.

The relationship between the percentage of dolomite in the carbonate portion of expansive rocks and the maximum expansion in percent is shown for 55 rocks in Figure 8. (Five points showing the maximum shrinkage of nonexpansive cylinders are included in the graph.) The graph shows that although there is no absolute relationship between expansion and dolomite content, most of the expansive rocks contain less than 40 percent dolomite and rocks containing less than 12 percent dolomite are usually not highly expansive.

Both the minor- and early-major-expansion groups have a wide range of dolomite contents from 4 to 78 percent and from 4 to 60 percent, respectively. Both groups therefore include limestones, dolomitic limestones and calcitic dolomites. However, almost two-thirds of the early-major-expansion group contained from 10 to 30 percent dolomite in the carbonate fraction and would therefore be classed as dolomitic limestones. Three of the early-major-expansion limestones contained less than 8 percent dolomite in the carbonate portion, making little dolomite available for dedolomitization, which is a part of the alkali-carbonate reactivity (8).

The five late-expansion cylinders are all calcitic dolomites with the very small variation in dolomite of 78 to 85 percent. This range might increase when more cylinders of this type are available for testing.

Percent Acid-Insoluble Residue.—The relationship between the amount of acid-insoluble residue found in the alkali-reactive carbonate rocks and the maximum expansion in percent for all cylinders is shown in Figure 9. The data indicate that all cylinders having maximum expansion of more than 0.5 percent fall within the range of 8 to 30 percent of insoluble residue and are therefore classified as impure carbonate rocks. Four of the early-major-expansion cylinders contained 20 to 30 percent of in-
Figure 8. Dolomite in percent of carbonate portion vs maximum expansion: cross = non-expansive cylinder, empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.
Figure 9. Acid-insoluble residue vs maximum expansion: empty circle = minor-expansion cylinder, solid circle = early-major-expansion cylinder, solid square = late-major-expansion cylinder, and C. B. = cylinder broke.
soluble residue and all five late-major-expansion cylinders were characterized by the very narrow range of 25 to 30 percent of noncarbonate constituents; thus one-quarter of the major-expansion groups had 20 to 30 percent of insoluble residue. Although the minor-expansion group covered a range from 2 to 24 percent of insoluble residues, most of the samples belonged to pure or relatively pure carbonate rock varieties.

No sample of Gull River rocks which contained more than 30 percent of residue showed expansion. At the other end of the scale, one sample with less than 5 percent dolomite, which showed rapid initial length increase but broke after 4 wk of testing, had only 4 percent of impurities and therefore represented a pure limestone (see Appendix—"Cracking").

Noncarbonate Constituents. — The X-ray analyses of the acid insoluble residues, performed by R. Laakso on 40 expanding samples, showed that all expanding rock groups contained illite, chlorite and quartz. Illite usually was the most abundant, but in a few samples, quartz was the most abundant, noncarbonate mineral. (It may be significant that the 10Å illite peak on the diffractometer trace was asymmetrical toward low angles in most samples. On heating, a sharper, more intense and symmetrical peak resulted. The asymmetry is probably due to significant hydration of illite (R. Laakso).) In each sample illite was present in larger amounts than chlorite. Potash feldspar was, in general, more abundant than plagioclase, but both feldspar types were usually present in very small amounts. The amounts of clay minerals and/or clastic grains are, of course, reflected in the amounts of insoluble residues, but they do not seem to be related to either the amount of dolomite or the degree of expansion.

Some of the expanding samples contained an expanding type of clay mineral. It is, however, unlikely that this mineral is responsible for the expansive properties of the rocks because it is present in very small amounts and no relationship could be established between its presence and the degree of expansion. Furthermore, this mineral was more frequently absent than present in the early-major-expansion group.

The late-major-expansion group with a relatively high noncarbonate content showed greater uniformity in noncarbonate mineral composition than the other groups. It was characterized by approximately the same amounts (medium to high) of illite and quartz, medium amounts of chlorite, and very small amounts of feldspars and of an expanding clay mineral.

These findings are similar to those reported by Gillott for rocks from the two Kingston quarries. No direct relationship was found between reactivity and composition (2, p. 771).

Texture

A fine-grained and relatively uniform texture is reported to be one of the deciding factors in determining whether a rock is alkali reactive or not. As described and illustrated in photomicrographs by Gillott (3) and Newlon and Sherwood (7), the expansive rocks are partially dolomitized calcilutite containing isolated dolomitic rhombs in a matrix of microcrystalline calcite and clay. This feature also appertained, in general, to highly expansive rocks of the Gull River formation belonging to the early-major-expansion group, but detailed examination of the numerous expansive rocks showed that their texture is quite heterogeneous on the thin section scale. The dolomitic rhombohedrons vary in size in different specimens and frequently in the same specimen. In the latter case, the presence of two generations of dolomitic rhombohedrons is indicated. The dolomite may occur more or less evenly distributed, or in patches or lenses, or it may be more concentrated in layers which may also be richer in clay minerals and/or clastic quartz grains. In some instances the concentration is so narrow and well defined that it may be referred to as a dolomitic clayey stylolite along which the cylinders are apt to break during NaOH immersion, as described in the Appendix.

The occurrence of fine clayey trains varying in size and concentration is typical for most of the major-expansion cylinders (Fig. 10). These stylolites, practically devoid of dolomite, may represent the formerly evenly distributed clayey and organic material that concentrated during dolomitization of the rock. They are, however,
usually not so pronounced as to prevent the preparation of cylinders perpendicular to the direction in which they extend and to the general sedimentation layering. It might be expected that these clayey concentrations open the texture of the rock in a direction perpendicular to their main expansion and thereby contribute to the expansion of the rocks in concrete. This would explain why cylinders and prisms cut parallel to the layering show a lower degree of expansion in the direction of their longitudinal axis (Table 1, Sample 1728 in the Appendix). Although gradations in the texture from a very fine-grained uniform lithographic variety to heterogeneous, fossiliferous and/or pseudooolitic varieties are noticeable, a simple relationship does not seem to occur between the textural particularities described and the degree of expansion.

The texture of the late-major-expansion rocks, which are classified petrographically as silty-argillaceous calcitic dolomites (Fig. 11), closely resembles that developed in areas of dolomite and clay concentrations visible in thin sections of the early-major-expansion group (see Figs. 10 and 12—Appendix). It is similar to the texture described in detail by Gillott (3) for the slightly reactive rock occurring in the 24- to 30-ft section of the Kingston quarry. In the late-expansion group very finely crystalline euhedral dolomite aggregate contains larger dolomite rhombohedrons (about 0.1 mm in size) as well as evenly disseminated coarse-sized silt grains of quartz (about 0.05 mm in diameter) and scarce rounded quartz grains in medium sand size (0.5 mm). The matrix between these minerals is formed by argillaceous material and very fine-grained calcite. The latter may occur also in the form of larger-grained patches containing small dolomite euhedra. For one late-expansion sample, the amount of quartz grains was distinctly lower and that of the argillaceous matrix correspondingly higher in comparison with another sample that had the same percentage of insoluble residue.

Future Work

The work is proceeding by testing additional samples in order to correlate the expansion of the small cylinders with that of large specimens equal in volume to Swenson and Gillott’s prisms (8).
In an attempt to correlate the expansion of concrete made of expanding Gull River aggregate with the expansion of the small cylinders in NaOH, large block samples of the carbonate rocks were obtained. After small test cylinders from along the whole cross-sections of the blocks are prepared, the material will be crushed and used as aggregate in concrete specimens.

**SUMMARY**

The carbonate rocks from the Gull River formation, suspected of being alkali reactive, were tested in NaOH solution in the form of small cylinders. Samples showing more than 0.1 percent of expansion were classified as expanding rocks and divided into three groups based on the amount and time of the maximum expansion observed: the minor-expansion group with less than 0.40 percent expansion, the early-major- and the late-major-expansion groups with at least 0.40 percent expansion. The maximum expansion found in the samples tests for 1 to 2 yr was 3.5 percent, but in a cylinder on which the test was recently begun, expansion has reached 4.4 percent in 26 wk.

The early-major-expansion group which usually showed distinct expansion in the first 2 to 5 wk consisted of dolomitic limestones, some calcitic dolomites and a few limestones proper. Inasmuch as this group contains rocks with from 3 to 30 percent of acid-insoluble residues, carbonate rock varieties ranging from pure to distinctly argillaceous and occasionally quartzose silty varieties were present.

Distinctly expanding calcitic dolomites, which started to expand after at least 25 wk of NaOH immersion, were contained in the late-major-expansion group. This group was much less abundant than the other two and its petrographic characteristics were much more uniform. It was characterized by more than 75 percent of dolomite and by 25 to 30 percent of noncarbonates. The late-major-expansion cylinders continue to expand after 2-yr immersion in NaOH and expansion measurements are still being made on this group of samples. The maximum expansion at the last reading was more than 1 percent. Any material in this class might be suspected of causing alkali-aggregate reaction in concrete made with high alkali cement and exposed to humid conditions. Detection of the late-expansion group is somewhat simplified because, assuming relatively complete sampling, the data indicate that material in this group always occurs
at locations in which material showing early-expansion of minor or major proportions is also present. Thus, in the cases investigated, the existence of a problem requiring corrective action would have been detected by early expansion results. However, the existence of the late-expansion group eliminates the possibility of early detection of the expansion characteristics of individual layers, which in some cases may be necessary if selective quarrying operations were to be considered in an attempt to avoid the problem.

The minor-expansion group comprised about one-half of the expanding cylinders. Rocks having this characteristic were found in all locations where the major-expansion layers occurred and also in a few quarries in which the latter were not detected. Petrographically, the minor-expansion group was rather heterogeneous and covered approximately the same range of petrographic properties as the major-expansion rocks. It has to be emphasized that not all cylinders showing little or no expansion in the first 2 or even 5 wk belong to this group, because such cylinders may later expand and be classified in the major-expansion group; or they may even decrease in length and may not be really alkali reactive. The significance of this group as far as volume changes in concrete are concerned has not been established, but such rocks may add to the expansion of concrete when included with highly expanding rock varieties.

No principal difference in the type of noncarbonate minerals was noticeable in the three expansive groups. Although the clay minerals were usually the most abundant constituents, quartz may be a relatively abundant constituent especially in the late-expansion group.

The texture of the expansive carbonate rocks varied from lithographic with dolomitic and argillaceous stylolites developed in limestones to microcrystalline in dolomites. Expanding carbonate rocks from the Gull River formation are concentrated in the Kingston area (six locations) but also occur in two locations outside of this area.

ACKNOWLEDGMENTS

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REFERENCES

Appendix

Detailed Observations on Cylinders

Cracking.—Cracking and chipping of the test cylinders are relatively common phenomena, especially in the early-expansion group. However, only four cylinders, three of them belonging to the early-major-expansion group, broke at an early testing age. In this regard one cylinder was interesting because it showed the effect of a clayey-dolomitic seam or stylolite (1.0 mm in thickness) occurring in a pure lithographic limestone (calcilutite, Fig. 12). The rock contained 4.1 percent dolomite and 4.7 percent insoluble residue. The cylinder expanded almost one-half percent in 4 wk, then the top cone, 0 to 2 mm in thickness, broke off along the slightly inclined stylolite. The somewhat shortened cylinder (1.0976 in. in length), with a reworked cone, consisted practically of pure limestone only and did not expand during the subsequent 40-wk immersion in NaOH.

The location and type of cracking appear to be correlated with some textural features of the rock as shown above. But neither the number of cracks nor their depth is directly related to the intensity of expansion or to the amount of noncarbonate impurities, as shown in Figure 13 by cylinders photographed after different periods of immersion. Whereas cylinder A (1728) with the greater expansion showed a hardly noticeable crack, cylinder B (1729), which expanded considerably less, developed numerous cracks which continued to increase in length and depth. The directions of the cracks were influenced to a great extent by the seemingly brecciated texture of the rock and the presence of stylolitic seams as shown by the thin section made of this sample and illustrated in Figure 10. Both cylinders reached almost the maximum expansion at the time the last photograph was taken.

The last cylinder, C, (Fig. 13) had a length increase of 3.6 percent after 7 wk of immersion. The cylinder is bent and shows an irregular pattern cracking. This cylinder, consisting of a greenish dolomitic limestone (11.5 percent insoluble residue),

Figure 12. Pure lithographic limestone with dolomite-clay stylolitic concentrations; early-expansion type (39X).
Figure 13. Cracks in expanding cylinders: (a) insoluble residue, in percent; (b) time of NaOH immersion, in weeks; (c) expansion, in percent.
did not break although it expanded 4.4 percent in 26 wk, the highest expansion value obtained to date on Gull River rocks.

Pairs of Cylinders.—Pairs of cylinders from the same sample usually gave similar expansion values within the limits of measurement error. In the minor-expansion group one of a pair of cylinders might not reach the lower limit of significant expansion (0.1 percent) and such cylinders therefore would be considered nonexpansive. The maximum expansion values of four major-expansion pairs with larger than usual differences within the pairs are given in Table 1. They demonstrate the heterogeneity of the samples that seemed megascopically rather uniform.

The difference in the expansions of cylinders cut parallel and perpendicular to sedimentation layering, is already well known (8) but may be normally much less than shown in the first pair (1728). The difference in the maximum expansion of the second pair (1729) might have been much greater if the more strongly expanding cylinder had not broken after 19 wk of immersion. The third pair (1874) represents a late-expansion rock (Curves 1 and 2, Fig. 5) and shows the slower rate of expansion in one cylinder in comparison with the second. The fourth pair (1882) belongs to the early-expansion group, as do the first two pairs. Because both cylinders were cut parallel to the layering, the maximum expansion of the rock might be greater than registered by these two cylinders.

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1Cylinder drilled parallel to layering.
2Cylinder drilled at right angle to rock layering.