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Alkali reactivity of dolomitic limestone aggregate

by E. G. Swenson and J. E. Gillott

Price 25 cents OTTAWA May 1967 NRC 9552

Réaction des agrégats de calcaires dolomitiques au contact des bases

SOMMAIRE

L'auteur a obtenu des preuves supplémentaires confirmant l'hypothèse selon laquelle le gonflement excessif des agrégats de carbonates soumis à l'action des bases serait causé par l'imbibition de la fraction argileuse anhydre. La réaction de dé-dolomitisation ne paraît nécessaire qu'en raison des besoins en humidité de l'argile enserrée. L'auteur a employé une méthode utilisant le microscope pour la détermination de la surface spécifique de la dolomie sous cette forme, dont les valeurs numériques ont permis de définir pratiquement une limite supérieure en dessous de laquelle il ne se produira pas de réaction entraînant de gonflement de l'agrégat.

L'auteur montre également que des pourcentages relativement faibles d'argile à illite peuvent causer le gonflement excessif affectant les agrégats de carbonates. Les nouvelles techniques employées comprennent la mesure des modifications de dimensions de plaquettes minces de roches et d'éléments compactés en argile ou en roche pulvérisée.

ĀNALYZED

Alkali reactivity of dolomitic limestone aggregate

by E. G. Swenson* and J. E. Gillott*

NATIONAL RESEARCH COUNCIL, CANADA: DIVISION OF BUILDING RESEARCH

SUMMARY

Additional evidence was obtained in support of the hypothesis that excessive expansion in the alkali-carbonate rock reaction is caused by moisture uptake by the previously 'unwetted clay' constituent. The dedolomitization reaction is shown to be necessary only to provide access of moisture to the 'locked-in' clay. A microscopic method was used to determine the specific surface of the dolomite, the quantitative nature of which made it possible to define a practical upper limit below which expansion does not occur. It was also shown that relatively small percentages of illitic clay can account for the excessive expansion shown by reactive carbonate rocks. The new techniques used included measurements of dimensional change of thin rock wafers and of compacts of clay and powdered rock.

Introduction

Excessive expansion and cracking of concrete occur when certain dolomitic limestones are used as coarse aggregate in conjunction with a high alkali cement. This is an alkali-aggregate reaction quite distinct from the alkali-silica type. Field problems involving the alkali-carbonate rock reaction were reported initially from parts of Canada [1-3] and the United States [4-6]. A symposium on the subject held in Washington in January 1964 [7] summarized the rather extensive studies that have been made since the problem was first uncovered in 1955.

There is generally good agreement about practical considerations involving the use of alkali-expansive carbonate rock aggregates in concrete. The compositional and environmental factors have been quite well established. Methods of identification have been developed, remedial measures have been determined, and

progress has been made in applying these to specifications and practice [3,8,9].

There is considerable disagreement as to the probable mechanism of expansion. Several hypotheses have been advanced. [4,10-13]

This paper describes a series of studies designed to test the hypothesis advanced by this laboratory [10]. Some new techniques were used, notably in determining specific surface of dolomite, in determining clay contents, in measuring changes in length of thin rock wafers through a special conditioning sequence, and in length-change isotherms of compacts of clay and powdered rock.

Experiments were carried out on a suite of over 40 carbonate rocks assembled from Canada and the United States, and supplied by recognized authorities in the field of alkali-carbonate rock reactions. Sampling was deliberately selective, the purpose being to include typical and non-typical expansive rocks as well as non-expansive rocks.

The hypothesis

There are three main characteristics of the expansive alkali-carbonate rock reaction in concrete. Expansive rocks have a characteristic composition and texture: they are fine-grained dolomitic limestones or calcitic dolomites [11,14]. Secondly, the dolomite constituent is chemically attacked by the cement alkali. This so-called dedolomitization reaction results in the formation of brucite, alkali carbonate and calcium carbonate [2,4]. Thirdly, there is an uptake of moisture accompanying the reaction. [1,3,10,15,16] A postulated mechanism of expansion should utilize and account for this evidence.

The water content of an aqueously deposited sediment is steadily reduced as the material is rendered less porous and more dense during its conversion into a rock by consolidation and lithification. Burial to

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depths of the order of a mile within the crust is considered reasonable for sedimentary rocks as old as the dolomitic limestones from Kingston, Ontario, which belong to the Ordovician system. (A Kingston, Ontario, limestone was the first to be identified with alkali-carbonate rock reaction.) It may be readily calculated that a pressure of the order of 60,000 lb/in^2 would be exerted on rock buried at a depth of $1\frac{1}{2}$ miles. On the basis of energy considerations, Van Olphen (reference 17, pp. 148–149) concluded that this is the equivalent pressure required to remove water within the last few monolayers from a clay mineral surface. Forces of a chemical nature and rise in temperature due to burial to considerable depth have to be considered, in addition to the pressure exerted during consolidation, in evaluating the energy available for expulsion of water from the mineral surfaces in rocks of this type. The inevitable conclusion is that these processes expel a large proportion of the water with which the minerals were associated at the time of deposition. Once this has occurred, the clay minerals may remain in a 'virgin', 'dry state', if they have become permanently inaccessible to moisture, having been enclosed or 'locked in' within the interlocking dolomite and calcite crystals that compose the skeletal fabric of the carbonate rock. Some of the clay would have been accessible to moisture and would have been pre-wetted.

It is postulated that the excessive expansion occurring in the alkali-carbonate rock reaction is produced directly by the uptake of moisture by the 'active' or 'virgin' clay[8,10]. The clay becomes exposed and accessible to moisture owing to the attack by the alkali upon the dolomite (dedolomitization), which opens up the originally tight fabric to penetration by moisture. It is further postulated that the clay in some such rocks has been always accessible to moisture, because of the particular physical state of the solid, and that such rocks are not expansive.

Results of experiments

SPECIFIC SURFACE OF DOLOMITE, CLAY CONTENT AND POROSITY

It was considered necessary at first to re-examine the parameters generally accepted as characteristic of potentially alkali-expansive carbonate rocks. These diagnostic criteria are:
  (1) abundant, fine-grained dolomite (dolomite with a high specific surface);
  (2) adequate content of clay;
  (3) low porosity.

Determining the specific surface of dolomite

The crystal size distribution of dolomite was obtained microscopically by actual count. Wherever possible, 300 crystals were counted in each slide. A graph was then constructed for each rock with crystal count plotted against crystal size in microns. The types of
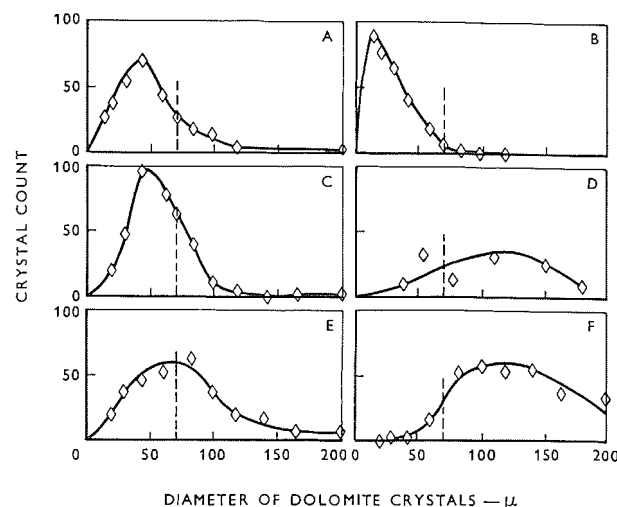

Figure 1: Size distribution of dolomite crystals in carbonate rocks.

curve obtained are shown in Figure 1 and will be discussed later.

The approximate surface area of the dolomite crystals per gram of rock (dolomite specific surface expressed in cm^2/g) was calculated from the dolomite content of the rock and the size distribution of the crystals. These data are recorded in Table 1. To simplify calculation, the dolomite crystals were treated as spherical particles with the short axis of the crystal taken as the diameter.

In attempts to relate expansive reactivity to dolomite specific surface, attention was given to the methods used for deriving the percentage of dolomite in a carbonate rock. Normally it is calculated from the chemical analyses on the assumption that all the magnesium is present as a constituent of the dolomite. One method used in this laboratory to check this assumption consisted of measuring the change in rates of evolution of carbon dioxide when acid is added to a uniform particle size of the rock.[18] The results on 16 samples recorded in Table 1 show good agreement.

Determining the clay content

The clay fraction was considered to be material smaller than 2μ (equivalent spherical diameter) found in the acid-insoluble residue. Separation of this residue was made with cold 1:1 HCl and water, stirred for $1\frac{1}{2}$ h. The residue was washed free from chlorides. In each case, it was dispersed in water to which had been added 5·1 g/l. of calgon (sodium hexametaphosphate). Other pre-treatments such as are often used for the removal of organic material (e.g. with H_2O_2), iron, and aluminium compounds[19,20] were not used, as it was desired to retain particles in a state as close as possible to that in the original rock. The $<2\mu$ fraction was separated by a standard sedimentation procedure and the percentage of clay in the original rock was calcu-

TABLE 1: **Compositional features of selected carbonate rocks and their expansion in 2M NaOH (prisms).**

Sample	Dolomite content of rock		Specific surface of dolomite (cm²/g)	Clay content* (%)	Porosity (%)	Expansion of prisms	
	Calculated from analyses	From CO₂ evolution				% at 9 weeks	Rating
1	51·5	—	316	9·8 (22·2)	0·9	0·137	expansive
2	51·1	57·4	285	3·6 (15·0)	4·0	0·515	very expansive
3	65·2	—	260	2·7 (27·3)	6·6	0·600	very expansive
4	52·3	—	248	14·7 (24·0)	13·3	−0·018	non-expansive
5	61·0	73·5	245	16·1 (23·7)	11·8	0·230	expansive
6	57·7	—	244	6·7 (15·1)	3·2	0·070	moderately expansive
7	37·1	41·8	239	2·0 (8·1)	1·4	1·190	very expansive
8	34·6	—	229	3·9 (10·7)	3·6	0·295	expansive
9	65·9	75·1	229	7·7 (15·0)	12·0	0·030	slightly expansive
10	44·2	68·9	218	4·1 (12·3)	5·8	0·830	very expansive
11	50·0	—	209	2·0 (25·1)	1·2	0·785	very expansive
12	44·9	46·1	194	2·4 (4·2)	0·7	0·385	very expansive
13	45·3	—	191	8·0 (7·1)	1·4	1·790	very expansive
14	34·1	38·4	163	12·9 (20·0)	1·5	broke	very expansive
15	39·9	—	156	1·3 (3·9)	0·5	0·037	slightly expansive
16	35·2	—	154	2·0 (7·0)	1·0	1·030	very expansive
17	36·2	—	151	22·7 (51·6)	3·9	0·015	slightly expansive
18	30·4	—	140	4·9 (11·8)	2·3	1·570	very expansive
19	29·6	—	129	2·0 (9·6)	10·1	0·260	expansive
20	31·6	—	127	4·2 (26·6)	2·4	0·530	very expansive
21	25·4	25·2	104	2·5 (5·7)	3·3	0·263	expansive
22	19·3	—	92	8·0 (14·4)	1·7	broke	very expansive
23	15·4	—	65	3·3 (10·0)	0·6	−0·010	non-expansive
24	12·2	—	59	3·0 (17·6)	0·8	0·188	expansive
25	13·9	—	59	1·1 (3·2)	0·6	0·001	non-expansive
26	13·8	—	53	1·9 (3·6)	0·4	0·000	non-expansive
27	9·5	19·6	41	2·7 (11·7)	5·9	0·157	expansive
28	6·9	4·3	41	5·1 (7·0)	0·6	0·140	expansive
29	8·9	—	38	4·4 (16·9)	1·1	0·103	expansive
30	7·6	—	35	2·1 (6·4)	1·2	0·322	very expansive
31	6·5	—	34	3·0 (6·1)	0·8	0·042	moderately expansive
32	6·5	—	30	0·5 (2·9)	1·8	0·038	slightly expansive
33	6·1	3·5	30	5·4 (7·9)	1·0	0·048	moderately expansive
34	4·5	0·4	21	6·8 (7·3)	1·6	−0·047	non-expansive
35	6·6	4·0	16	1·7 (5·5)	0·4	−0·018	non-expansive
36	3·0	3·2	15	6·5 (7·4)	0·3	−0·019	non-expansive
37	2·7	—	10	3·2 (4·9)	0·8	−0·027	non-expansive
38	44·6	30·5	0	10·9 (19·7)	1·1	0·000	non-expansive
39	41·3	—	0	1·1 (1·4)	1·3	0·004	non-expansive
40	4·9	1·1	0	1·1 (4·6)	1·2	−0·024	non-expansive

* The values in parentheses are the percentage of insoluble residue.

lated. The data for the 40 rocks are given in Table 1 for discussion below.

Determining the porosity

From vacuum saturation data, the apparent porosity was obtained as the ratio of the volume of voids to the total volume of the solid, calculated as percentages. Care was taken to use pieces of rock that were free from cracks and pockets but it was not certain that this was achieved in every case. Again the results are recorded in Table 1 for subsequent discussion.

RESULTS OF EXPANSION TESTS ON ROCK PRISMS

From each rock, prisms measuring $2 \times \frac{1}{2} \times \frac{1}{2}$ in. were cut. They were immersed in 2M (molar) NaOH solution and the lengths measured periodically by means of a dial extensometer that measured to the nearest 0·0001 in. Expansion after 9 weeks was taken as the measure of expansive reactivity, although early cracking was taken into account in establishing a rating. The linear dimensional change results and the ratings are recorded in Table 1. A word of caution is necessary for those not familiar with length measurement on expansive concrete prisms and reactive rock prisms immersed in alkali. Visible cracks appear in concrete prisms when the percentage linear expansion reaches about 0·05 to 0·08. In rock prisms, cracking may first appear from very low to very high expansions—as high as about 0·2 %. Once cracking starts, there is mechanical separation and, therefore, length change data after this point must be used only qualitatively.

DISCUSSION OF CORRELATION IN TABLE 1

Low porosity apparently is not a necessary characteristic for excessive expansion of reactive rocks in alkali solution. This is evident from the rather poor correlation between porosity and expansion in Table 1. Where aggregates are subjected to high restraining forces imposed by hardened cement paste, however, it is possible that highly porous rocks that expand in alkali will not produce significant expansion in concrete.[2,3]

The quantity of clay present shows no correlation with expansion. The results confirm those of previous studies, however, that clay is always associated with expansive reactivity in a carbonate rock. These results and others previously obtained in this laboratory indicate that clay contents as low as 2% are sufficient for high expansion of the rock. This is contrary to concepts reported elsewhere[11], in which an attempt is made to correlate an increase in clay content with increased expansivity. It was postulated that the clay caused disruption of the carbonate skeleton, thus weakening the resistance of the rock to expansive forces. This may be a factor but is apparently not a major one.

Good correlation is obtained between expansive reactivity and specific surface of the dolomite. This is first indicated by the type-curves of Figure 1 showing size distribution of dolomite crystals. Figure 1a, sample 11, is an example of a highly expansive rock in which most of the dolomite occurs in the $<70 \mu$ range. A size boundary of 70 μ is chosen on the basis of observations made in a dilatometer study of powdered rocks.[10] Figure 1b, sample 10, is a case where the crystal count reached a maximum at the minimum size at which it was possible to resolve microscopically for accurate measurement (10 μ). In these instances the curves were extrapolated, but it was quite evident that such samples should be reactive. In fact, they are shown to be highly expansive (Table 1). Figure 1c, sample 15, shows a smaller proportion of the crystals in the $<70 \mu$ range. Such a sample should be only moderately reactive, and Table 1 shows that it is slightly expansive.

Figure 1d, sample 37, illustrates a case where the dolomite crystals can be predicted to be too coarse to be reactive. Table 1 shows this sample to be non-expansive in alkali, although the low dolomite content may be a contributing factor. Figure 1e, sample 26, shows an approximately even distribution on each side of the 70 μ line. The sample might be expected to be slightly reactive and is shown to be non-expansive (Table 1). Figure 1f, sample 9, is a case where the specific surface of the dolomite is very high (229 cm²/g), mainly because of the high dolomite content, but the sample is only slightly expansive because the crystals are mainly coarse.

In Table 1 it is noted that rocks with a specific surface greater than 100 cm²/g of rock all show excessive expansion, with one exception, sample 4. This exception is attributed to the clay having been pre-wetted.

Samples with a dolomite specific surface of less than 30 cm²/g did not show abnormal expansion. Those with values between 30 and 100 cm²/g appear to be a borderline group, some being expansive and others not.

Considerable reference has been made elsewhere to the significance of the dolomite to calcite ratio. The suggestion has been made that the most expansively reactive rocks contain approximately equal percentages of dolomite and calcite[2,4,11,21]. On the basis of results from our studies, it would appear that specific surface of the dolomite is the significant factor, provided enough dolomite and clay are present. Increased dolomite specific surface would increase the rate and degree of dedolomitization, which would result in increased rate and degree of expansion if 'active' clay were present. It can be seen from Table 1 that this generally means increasing expansive reactivity with increasing dolomite content, except when the dolomite grain size is too coarse. The apparent exceptions are samples 38 and 39 in which it is not possible microscopically to identify the dolomite for counting purposes. Hence, the zero values for dolomite specific surface are arbitrary.

The condition and the role of calcite have been given importance by some researchers[11,22]. In our studies involving about a hundred carbonate rocks, both expansive and non-expansive, every expansive rock has contained considerable very finely divided calcite. This material has been associated with an acceleration of dedolomitization[11] and with direct contribution to expansion[13,22]. In our hypothesis, the finely divided dolomite is associated with the even more finely divided calcite in providing a system in which the clay can be permanently inaccessible to moisture, unless exposed by dedolomitization or heating.

VOLUME CHANGES IN THIN ROCK WAFERS

The role of the clay fraction was examined further by measuring the volume change response of thin rock wafers, selected from rocks with different clay contents and known reactive expansivities based on prism tests. These wafers, measuring 1·25 × 0·25 × 0·05 in., were inserted into small, optical extensometers which measure length change to 0·00005 in.[23] Each loaded extensometer was placed in a special conditioning cell in which the environment ambient to the sample could be varied. The cell could be evacuated, conditioned at any relative humidity, or flooded with water or alkali solution (Figure 2). This method of measuring length change made possible the rapid attainment of equilibrium, yielded greatly improved reproducibility, and permitted much better control than is possible with the usual rock prism methods.
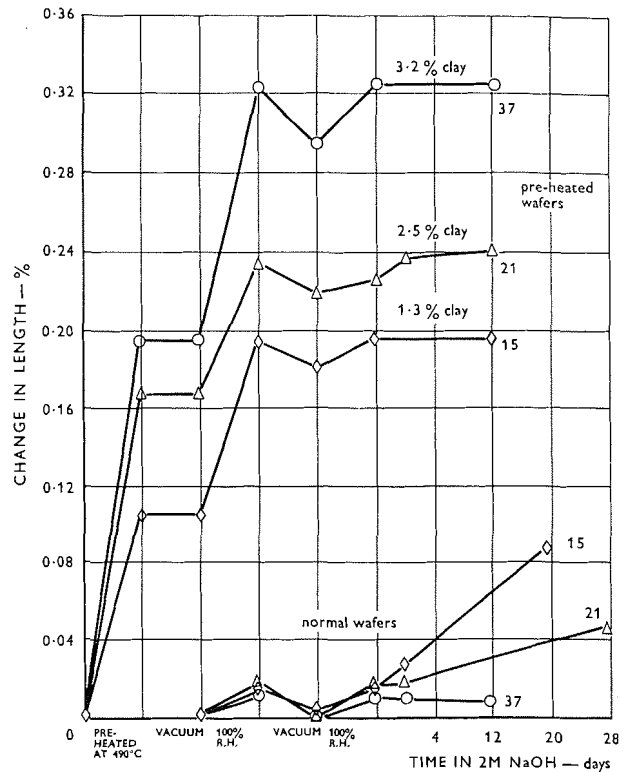
Figure 2: *Conditioning cell with optical extensometers and mounted samples.*

Figure 3: *Effect of pre-heating on dimensional changes of expansive and non-expansive carbonate rocks.*

Sample	Description	Clay content (%)
15	Expansive in prism test	1·3
21	Expansive in prism test	2·5
37	Non-expansive in prism test	3·2

Following preliminary probe runs with various sequences, the procedure adopted was to evacuate the sample, subject it to 100% relative humidity (R.H.), evacuate it again, expose it to 100% R.H. again, and finally immerse it in 2M NaOH. The time taken for each step in the sequence was determined by the equilibrium value for length change. All experiments were carried out in a conditioned room at 21°C.

Length-change response to the above sequence was determined on normal rock wafers and on companion wafers that had been pre-heated to 490°C for 3 h and cooled to room temperature before testing. The pre-heating was intended to expose previously unwetted clay in the rock without basically altering its structure, by causing internal micro-cracking. This heat treatment was presumed to be not enough to decompose either the dolomite or the calcite components in the rock.

The results of these equilibrium length-change measurements are given in Table 2. The significant features of these data are best illustrated by the plots in Figure 3 for two expansive rocks, 15 and 21, and for a non-expansive rock, 37.

The lower set of curves for the normal rock wafers (not heated) in Figure 3 shows a small, essentially reversible length change between vacuum and 100%

R.H. This is attributed essentially to the finely divided carbonate material. Samples with higher clay contents yielded greater length changes, presumably because of some contribution made by clay already accessible to moisture (e.g. 6, 4 and 17 in Table 2). Immersion in 2M sodium hydroxide solution yielded expansions in general agreement with those obtained with the larger prisms, but with significant differences in magnitude. Of the six expansive rocks tested, two (15 and 29) expanded more in the wafer test; the others expanded more in the prism test. These results confirm an observation made previously in this and other laboratories that wide variability in degree of reactivity may occur in any given rock. This has already led to practical recommendations that comprehensive sampling in a quarry is essential when the rock prism test is used to evaluate coarse aggregate.

The upper set of curves in Figure 3 shows the corresponding length changes for wafers from the same three rocks but which had been pre-heated to 490°C for 3 h and cooled to 23°C. This treatment resulted in large irreversible expansions of the rock wafers (Table 2). The linear coefficients of thermal expansion are given by [25]

$$\alpha' = \frac{10^6}{l} \frac{dl}{dt} \text{ at } t°$$

99

TABLE 2: **Length changes of wafers of selected carbonate rocks subjected to various treatments.**

Sample	Dolomite content	Calcite content	Clay content	Expansion rating from prisms	Expansion of heat-treated samples (%)	Expansion with change in R.H. (%)			Expansion in 2M NaOH (%)	
	(% of total rock)					Vacuum to 100% R.H.	100% R.H. to vacuum	Vacuum to 100% R.H.	24 h	Total
41	99·1	1·3	none	non-expansive	— 0·432	0·004 0·010	— 0·002	— 0·002	0·000 —	0·004 —
42	98·2	2·3	none	non-expansive	— 0·415	0·012 0·048	— 0·006	— 0·006	0·000 0·004	0·000 0·010
43	91·2	3·3	—	non-expansive	— 0·176	0·012 0·006	0·008 0·006	0·008 0·006	0·008 0·004	0·012 0·014
6	57·7	26·8	6·7	expansive	— 0·141	0·004 0·074	0·044 0·056	0·044 0·054	0·006 0·008	0·020 0·002
4	52·3	16·4	14·7	non-expansive	— 0·088	0·038 —	0·038 0·027	0·036 0·024	0·008 0·010	0·020 0·012
39	41·3	56·4	1·1	non-expansive	— 0·185	0·044 0·046	0·004 0·008	0·007 0·008	0·003 0·008	0·011 0·020
15	39·9	55·6	1·3	expansive	— 0·105	0·014 0·095	0·011 0·014	0·012 0·016	0·011 0·000	0·073 0
17	36·2	12·8	22·7	slightly expansive	— 0·088	0·090 0·106	0·085 0·086	0·087 0·082	— 0·032	0·016 0·046
18	30·4	55·1	4·9	expansive	— 0·106	0·032 0·064	0·031 0·022	0·031 0·023	0·010 0	0·033 0·006
19	29·6	60·2	2·0	expansive	— 0·159	0·023 0·028	0·020 0·016	0·018 0·006	0·008 0·004	0·026 0·010
21	25·4	68·5	2·5	expansive	— 0·168	0·016 0·068	0·016 0·016	0·016 0·008	0·002 0·010	0·028 0·016
29	8·9	73·7	4·4	expansive	— 0·088	0·018 0·146	0·012 0·058	0·014 0·040	— 0·024	0·132 0·034
44	8·4	92·0	none	non-expansive	— 0·141	0·012 0·036	— 0·006	— 0·008	0·002 0·010	0·002 0·020
40	4·9	91·7	1·2	non-expansive	— 0·353	0·016 0·032	— 0·014	— 0·010	0·000 0·004	0·000 0·002
37	2·7	93·1	3·2	non-expansive	— 0·194	0·011 0·128	0·011 0·028	0·010 0·030	0·001 0·000	0·000 0·001

or

$$\alpha = \frac{10°}{t} \frac{\Delta l}{\Delta t} \text{ over the range } \Delta t°$$

The linear coefficients of thermal expansion for calcite are $\alpha^{40} = 26·21 + 0·0160 (t - 40)$, parallel to the optic axis, and $\alpha^{40} = -5·40 + 0·0087 (t - 40)$, perpendicular to the optic axis; for dolomite, the linear coefficients are $\alpha^{40} = 20·60$ with $\Delta (20° - 70°) = 36·8$, parallel to the optic axis, and $\alpha^{40} = 4·15$ with $\Delta (20° - 70°) = 19·3$, perpendicular to the optic axis. It can be seen that these quantities vary considerably, both with direction in a single crystal and between the two components. Therefore, heat treatment would be expected to cause considerable differential stress within the rock, relief from which may have been achieved by internal distortion and micro-cracking. It is presumed that this is the cause of the irreversible changes in linear dimensions on heating and cooling back to room temperature.

The first exposure of the vacuum-dried samples to 100% R.H. produced a generally much greater expansion for the heat-treated than for the non-heated rock wafers, much of this expansion being irreversible in the case of the heat-treated samples (Figure 3). The greatest effect generally occurred with rocks containing considerable amounts of clay or with rocks containing considerable amounts of the finely divided calcite (Table 2). It is concluded that the heat treatment caused micro-cracking because of the drastic thermal expansion and that this exposed any clay which was previously 'locked in' and from which water had been expelled by consolidation and lithification, and which was therefore inaccessible to moisture. The heat treatment may also have dried that clay which was always in the 'exposed' state. Thus, on first exposure of the pre-heated samples to 100% R.H., the expansion will be due to the total clay plus the extremely fine calcite.

The expansion recorded is of the same order of magnitude as that registered by non-heated samples on immersion in 2M alkali. The lack of complete reversibility on drying the pre-heated samples after exposure to 100% R.H. may be attributed to interference between the grains of the carbonate rock skeleton. On re-exposure to 100% R.H. (Figure 3), the clay again expands to the limit of the original volume.

On final exposure to alkali, then, any further expansion could not be accommodated in void spaces within the skeletal rock fabric but should register as a measurable dimensional change. The fact that this does not happen indicates that the expansive potential has been exhausted under conditions that preclude a contribution from the chemical reaction between the dolomite and the alkali. In the pre-heated samples, de-dolomitization causes no significant expansion as there is no concurrent moisture uptake by newly released clay, the latter having already been exposed by micro-cracking.

Although the main dehydroxylation of illites occurs above 500°C[26], it is possible that some dehydroxylation did occur in the pre-heating treatment of the rocks. Loss of most of the hydroxyl water would increase the height of the unit cell of illite by 1 to 2%. Thus, dehydroxylation, if any occurred, should have contributed to the expansion on pre-heating. Re-hydroxylation, on the other hand, is very slow; if any occurred, it should have resulted in slight shrinkage, and therefore cannot account for all or even part of the expansion observed.

On the basis of the assumptions made above, it follows that the subsequent immersion in alkali solution of the heat-treated specimens should not produce significant expansion even for the most reactive rocks. This is borne out by the results given in Figure 3 and Table 2.

On immersion of the rock wafers in 2M sodium hydroxide, an initial, appreciable expansion in the first 24 h occurred for most of the rocks whether pre-heated or not. This was considered a wetting effect rather than one due to alkali, and should be taken into account when comparing the results in Table 2.

VOLUME CHANGES IN POWDER COMPACTS

The magnitude of the expansion of clay on wetting, when it is a constituent of a rigid porous system as in rock, cannot be determined directly. The powder compact, however, offers a system that can be subjected to various relative humidities and the corresponding length changes measured. The technique of making compacts has been reported previously[23].

In the first experiment, three sorts of powder were studied. The reference material was a standard Fithian illite clay. Most, if not all, of the clay present in expansive carbonate rocks has been shown to be illite.[4,14] The test material was taken from the acid-insoluble

component of an alkali-reactive and expansive rock; the residue had been separated by treatment with acid. Microscopic evidence showed that about half of this was smaller than 2 μ. The acid-insoluble residue was separated into two portions; one portion was flocculated in $CaCl_2$ solution to substitute Ca ions for H ions which had resulted from the acid separation, and the other portion was flocculated in NaCl solution in order to saturate exchange sites with Na ions. Exchange sites are likely to be occupied by Ca ions in a carbonate rock, but immersion in 2M NaOH would result in some degree of conversion to an Na system. Hence, the moisture uptake characteristics of clay saturated with both Ca and Na exchange ions were investigated.

The compacts were made at a pressure of 40,000 lb/in² and all had a porosity of about 15% as determined by a porosimeter. Wafers measuring 1·25 × 0·25 × 0·05 in. were cut from the compacts, mounted on optical extensometers, and placed in cells as previously described for rock wafers. The samples were subjected to a stepwise increase in relative humidity beginning with a vacuum-dried state. The equilibrium values for adsorption and desorption are plotted in Figure 4. In this and subsequent experiments, the zero condition was obtained by vacuum-drying over magnesium perchlorate to equilibrium length change. Equilibrium points were obtained only to 65% R.H. Beyond this, the samples were exposed for several hours to 75% R.H. but had to be returned to 65% R.H. because the very high expansions had gone beyond the range of the extensometers. Because of possible adverse effects on the integrity of the compacted sample, these samples were not taken to higher relative humidities. Denser specimens of these materials made at pressures of 110,000 lb/in² yielded expansions very nearly the same as the 40,000 lb/in² samples, and are therefore not reported here.

Subsequently, a compact of illite clay was exposed to 80% R.H., and its modulus of elasticity after exposure was found to be higher than before the exposure. Hence, the compacted material remained intact during this exposure.

From Figure 4 several significant observations can be made. The absorption curves for the three materials tested in one series are quite close together (solid lines). The sodium derivative was only slightly less expansive than the calcium clay up to 65% R.H. (The sodium sample was lost after this point.) The desorption curves of the two remaining samples indicate that the ultimate expansion at 100% R.H. would apparently have been much higher for the Fithian illite clay than for the residue. In the latter case it is possible that the physical structure of the clay is somewhat affected by the extraction with acid. It is noted, however, that the degrees of irreversibility of the samples of natural and extracted clays are essentially the same.

Adsorption-desorption isotherms for the two acid insoluble samples were also obtained. These were very
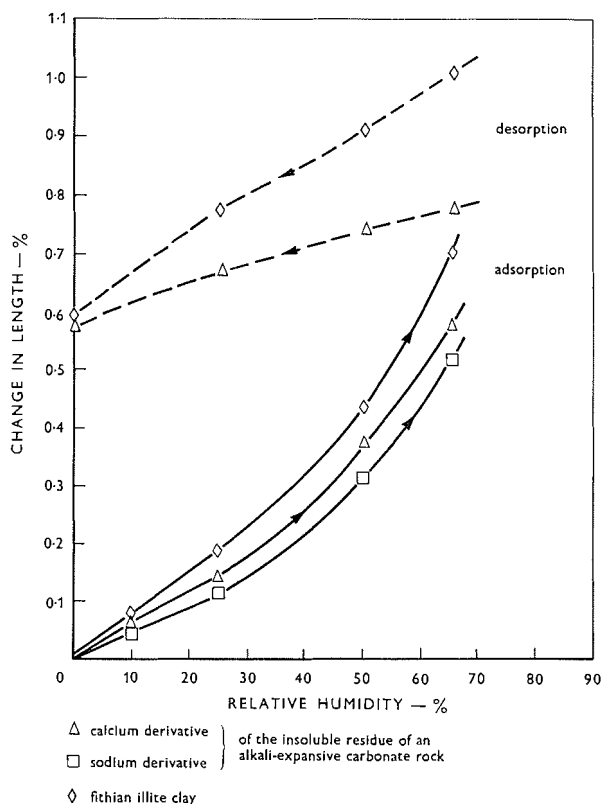
Figure 4: Partial isotherms for change in length of compacts of clay grade materials in carbonate rocks.

similar, showing a weight gain of about $7\frac{1}{2}\%$ at 90% R.H. The calculated specific surface area of the Ca-saturated acid-insoluble residue was $45\cdot5$ m^2/g and of its sodium derivative, $36\cdot4$ m^2/g.

It can be deduced from Figure 4 that, if these compacts of powders could have been measured safely up to saturation, the total linear expansion would have greatly exceeded 1% and probably would have exceeded 2%. Furthermore, expansion is measured parallel to the plane of the compact. Experiments have shown that dimensional change is considerably greater normal to the plane of such compacts. The results interpreted in the light of these considerations mean that there is present in illite clay (normally classed as not highly expansive), a potential for expansion in a solid system of a magnitude sufficient to account for observed excessive expansions of carbonate rocks containing relatively low clay contents. It suggests that the clay need only be in an initial 'dry' state to produce the expansive effects observed when it is 'exposed' to moisture through dedolomitization, heating, or other forms of micro-crack.

As a first approximation one might assume a value of 2% as the expansive potential of the clay, and calculate directly a predicted linear expansion of $0\cdot05\%$ in a rigid solid (rock) containing $2\cdot5\%$ clay. This is in the order of magnitude found to be excessive in carbonate rock used as coarse aggregate. There are, however, several considerations which suggest that the

calculated value in the above case is a minimum, and that the actual expansion can be expected to be considerably greater.

It has already been noted that cracking, which may start at relatively low expansions depending upon the modulus of the rock, would lead to a measured expansion much greater than the intrinsic expansion of the rock. Cracks tend to open up. This additive effect is doubtless present in most of the high expansion results of Table 1. A second factor is the contribution to expansion of material other than acid-insoluble in the 1 μ size range. This could be quite extensive and it can be expected that much of the calcite, and even some of the dolomite in the size range of 2 μ and less, will contribute to expansion in the same manner as the clay itself.

A third factor to consider is that the compact of clay, although a rigid, porous system, is much more porous than the natural rock (Table 1). The expansion of the clay in the rock may therefore produce a higher over-all expansion than in the case of the less dense compact. Finally, it is again noted from Figure 4 that the expansions of the clay materials were measured only to 65% R.H. and only in the plane of the compact. It is possible that the total expansions under saturated vapour conditions are much higher than the above conservative estimate of about 2%.

By means of a cell technique reported elsewhere[10,16], a volume increase of 7% was obtained on alkali treatment of the powdered form of the rock from which the above acid-insoluble residue was obtained. The acid-insoluble content is $10\cdot5\%$, about half of which is illite clay. This percentage increase in volume corresponded to a volume increase of about $0\cdot02$ cm^3/g of rock. On the assumption that the rock actually contained only 5% of clay grade material, calculation shows that the observed volume increase corresponds to $0\cdot4$ cm^3/g of clay present. If the volume increase resulted from water uptake by the clay, it is seen that the calculated value is in remarkably good agreement with a value of $0\cdot42$ cm^3/g moisture pick-up by calcium illite in $4M$ $CaCl_2$, reported in studies of volume increases in clays on moisture imbibition[27]. This is additional evidence that a small percentage of 'previously unwetted' clay of the illite type could account for the observed expansions in alkali-reactive rocks.

In a second series of experiments, compacts were made from powders of five different carbonate rocks previously studied (samples 15, 29, 41, 42, 44). All the powders were of approximately the same fineness, microscopic examination showing about the same size range of particles greater than 1 μ in diameter: 1 to 60 μ. The compacts were made by compacting the powders at $100,000$ lb/in^2 to porosities ranging from 17 to 19% (by porosimeter).

Wafers of these compacts were mounted on optical extensometers, and partial length-change isotherms on
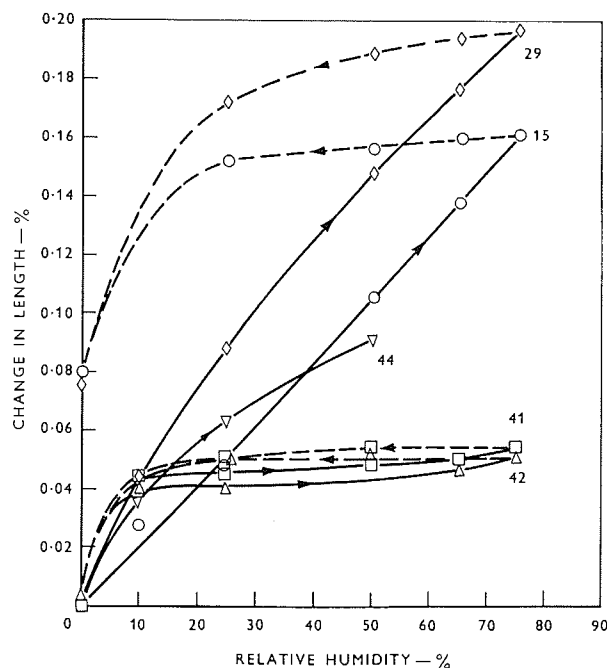
Sample	Description	Clay content	Dolomite content	Calcite content
			(% of total rock)	
15	Expansive	1·3	39·9	55·6
29	Expansive	4·4	8·9	73·7
41	Non-expansive	0	99·1	1·3
42	Non-expansive	0	98·2	2·3
44	Non-expansive	0	8·0	92·0

Figure 5: Partial isotherms for change in length of compacts of powdered carbonate rocks.

four of them were determined from equilibrium values at relative humidities of 10, 25, 50 and 75%. The fifth sample, No. 44, was tested in a separate experiment to 50% R.H. and dried directly to 0% R.H.; the results are plotted in Figure 5.

Samples 41 and 42 are essentially pure dolomites and sample 44 is highly calcitic, all three containing practically no clay (Table 2). Contrary to the behaviour of the clay, the volume change in each case is essentially reversible. As expected, the magnitudes of expansion are much less. than for the clay materials (compare Figures 4 and 5). The somewhat greater expansion of the calcitic sample 44 is attributed to a greater proportion of very fine particles. It is clear from these results that finely divided carbonate rock materials may contribute to some degree to the total volume change exhibited by an expansive rock, providing some of this material, as well as the clay, has been in a 'dry' state and inaccessible to moisture until exposed by the dedolomitization reaction or by micro-cracking.

The other two compacted powders are from alkali-expansive rocks Nos. 15 and 29. Their partial length-change isotherms in Figure 5 show a much larger expansion than for the non-expansive dolomites and

calcite (samples 41, 42, 44). The large hysteresis loops and the large irreversible portions are attributable to the clay and clay-like constituents (compare with Figure 4). It is noted that the expansion is higher for the sample containing the higher clay content. It is concluded from these results that the high expansions shown by these two samples are due largely to the clay present, but also to very finely divided calcite which is characteristic of alkali-expansive carbonate rocks.

It should be noted that a pressure of 100,000 lb/in² corresponds to about $2\frac{1}{2}$ miles of overburden. The compacts of powdered rock produced and used in these experiments have a porosity of 18%, but actual porosities of expansive rocks were generally much lower (Table 1). This clearly implies the action of additional processes in nature to yield the higher density of the rocks, as burial to the great depths required seems unlikely, according to a personal communication received from B. A. Liberty. Two such processes that are almost certain to have been involved are temperature rise and recrystallization. Ageing of finely divided materials in a rigid, porous system tends towards densification, too. These considerations are also pertinent to the argument that the magnitudes of expansion of the clay and powdered rock compacts represent minimum values. The less porous natural rock of the same composition should expand considerably more as a result of moisture pick-up by the clay and other finely divided materials.

The results of the experiments on the rock wafers and on the compacts of clay powders and powdered rock are considered strong supporting evidence for the hypothesis advanced by this laboratory.

Conclusions

Additional evidence was obtained in support of this laboratory's hypothesis as to the mechanism of expansion in the alkali-carbonate rock reaction. It is proposed that excessive expansion is caused by wetting of the clay and clay-like constituents that have been in the dry state and inaccessible to moisture until exposed by the dedolomitization reaction. This dry state results from the expulsion of water at the time of conversion of the sediment into rock during the geological processes of consolidation and lithification.

The methods and apparatus used were mainly new to this area of investigation. The rocks studied were specially selected for known expansivity.

A semi-quantitative correlation was obtained between the specific surface of the dolomite constituent of argillaceous carbonate rocks and their expansions in alkali solution as determined by the rock prism test. Thus, the extent of the expansive reaction is directly dependent upon the extent of dedolomitization, provided the other requirements are present, particularly the 'unwetted' clay. The method used here for determining specific surface of dolomite and the results it

yields have direct application in assessing carbonate coarse aggregate for concrete.

It was shown that carbonate rocks expand excessively in alkali solution, even though they may have quite low clay contents. Length-change isotherms of compacts of illite clay and the acid-insoluble fraction of an expansive rock demonstrated, however, that the potential expansion inherent in these materials is large enough to account for measured expansions in the rock.

Further evidence of the effect of the clay constituent in producing dimensional change was obtained from partial length-change isotherms of powdered carbonate rocks. These experiments also provided evidence that the more finely divided carbonate material, particularly the calcite, may contribute to expansion through uptake of moisture in the same way as the clay.

Pre-heating the normally expansive rock to 490°C rendered it non-expansive in alkali solution. The heat treatment was considered to have had essentially the same effect as dedolomitization in exposing previously unwetted clay and other finely divided materials to moisture access. The dimensional change characteristics of the heat-treated rock when exposed to saturated water vapour were taken as good evidence that the clay and clay-like constituents of the rock are directly responsible for the large expansion observed in expansive carbonate rocks. Other hypotheses do not account satisfactorily for these observations.

From the results obtained on the whole suite of specially selected carbonate rocks, it was possible to conclude, with a greater degree of assurance than before, that expansive rocks are invariably associated with a high dolomite specific surface, a clay constituent and considerable amounts of extremely finely divided calcite.

ACKNOWLEDGEMENT

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