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Changes in weight and dimensions in the drying and carbonation of Portland cement mortars

by K. Kamimura, P. J. Sereda and E. G. Swenson

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Variations de poids et de dimensions des mortiers de ciment Portland produites par le séchage et la carbonatation

Sommaire

De petits spécimens de mortier et de pâte (traités durant 28 jours) de perméabilité et de compressibilité variées ont été séchés avec carbonatation subséquente ou simultanée, à différents degrés d'humidité relative allant de 100 à 0%. On a ensuite séché les spécimens équilibrés afin de faire disparaître l'eau évaporable, puis on les a saturés de nouveau et séchés une autre fois pour déterminer la différence des réactions pour ce qui est des variations de longueur et de poids, et de la teneur en CO_2*. Quand ils n'étaient pas soumis à l'action du* CO_2*, les spécimens saturés, gardés dans une humidité relative de 50%, laissaient échapper un minimum d'eau non-évaporable et subissaient un retrait maximum en comparaison des spécimens équilibrés à d'autres degrés d'humidité relative. Soumis à une carbonatation subséquente, ces spécimens ont subi un retrait de carbonatation maximum près de deux fois supérieur au retrait dû à l'évaporation de l'eau. A 100% et de 25 à 0% d'humidité relative, la carbonatation n'a pas provoqué de variation de volume importante. L'action maximum de la carbonatation s'est manifestée chez les spécimens équilibrés à une humidité relative de 75%. En général, les résultats de la carbonatation, pour une concentration donnée de* CO_2*, dépendent de la perméabilité, de la teneur en humidité et du temps, mais l'importance du retrait dû à la carbonatation et la constance finale du volume dépendent de la compressibilité des agrégats, du rapport eau-ciment, de la maturité de la pâte, du milieu ambiant et de la vitesse du séchage, et des séquences de séchage et de carbonatation. L'auteur note quelques implications pratiques de ces résultats.*

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Changes in weight and dimensions in the drying and carbonation of Portland cement mortars

by K. Kamimura*, Ph.D., P. J. Sereda, M.Sc. and E. G. Swenson, M.Sc.

NATIONAL RESEARCH COUNCIL, CANADA: DIVISION OF BUILDING RESEARCH

SUMMARY

Small specimens of mortar and paste were cured for 28 days and then subjected to various conditions of drying and carbonation. In general the extent of carbonation, for a given CO_2 *concentration, depends upon permeability, moisture content and time, but the extent of carbonation shrinkage and ultimate volume stability depend on the compressibility of the aggregate, the water/cement ratio, the maturity of the paste, the drying environment and rate, and on the sequence of drying and carbonation. Some of the practical implications of these results are noted.*

Introduction

The significance of carbonation and carbonation shrinkage of Portland cement products has been of special interest to the Division of Building Research in its continuing studies of dimensional change in building materials. In Canada the extremes and variability of climate are conducive to wide changes in relation to humidity and, consequently, to moisture contents in materials. Because both drying shrinkage and carbonation shrinkage increase with decrease in relative humidity over the higher and intermediate ranges of humidity, and because the two effects are additive, the resulting large volume changes can, under certain conditions, lead to cracking, displacement, warping and related problems. The relative humidity in a heated building in very cold weather has been known to go well below 10%; in spring or summer it may approach 100% in the same building. Concentrations of carbon dioxide in heated, non-ventilated rooms can become high.

Field evidence of excessive shrinkage cracking that can be specifically traced to the added influence of carbonation is not well defined. This is doubtless due to a failure to recognize that the magnitude of carbonation shrinkage can approach that of drying shrinkage. The first-named author has, however, observed cases in Japan where both cracking and corrosion of reinforcement in lightweight concrete are believed to be due to carbonation of cement paste.

With dense concretes, drying and carbonation shrinkage are both normally small because of the low permeability of the concrete and the low compressibility of the aggregate. But over a long period of time the additional shrinkage resulting from carbonation can be critical for certain elements such as thin, prestressed units. Crazing of surfaces and warping of beams may also occur through carbonation.

Lightweight concretes are more susceptible to carbonation and its effects because they are usually more permeable. The problem of shrinkage is further aggravated by the higher compressibility of the aggregate.

The general irreversibility of changes in volume due to carbonation is beginning to be applied in the block and brick industry to pre-shrink masonry units by the " drying-carbonation " method.(1-3)

Research on carbonation and its effects on Portland cement paste, mortar and concrete has been summarized up to 1956 by Lea.(4) Subsequent investigations have been reported by Verbeck(5), Leber and Blakey(6), Kroone and Blakey(7), Alexander and Wardlaw(8), Hunt and Tomes(9), and Powers(10). The present state of knowledge may be briefly summarized as follows.

Substantial carbonation occurs even at the low CO_2 concentrations normally found in the atmosphere. It is not limited to the hydroxides present, but is also associated with other components in the paste. The resulting modification of the cement gel is reflected in certain changes in properties. Except at early ages, strengths are improved. Hardness, impermeability, and volume stability are favourably affected. The most dramatic effect of carbonation, however, is the large

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increase in shrinkage under intermediate conditions of relative humidity. Maximum carbonation and carbonation shrinkage occur at about 50% relative humidity (R.H.). Some carbonation but no carbonation shrinkage occur at 100% and at 25% R.H. Below 25% R.H. there is some disagreement. Carbonation shrinkage is a separate phenomenon from drying shrinkage and is superimposed upon the latter. It is largely irreversible, as compared with shrinkage due to loss of water. The size and permeability of the specimen and the concentration of CO_2 are rate-determining factors. There is considerable evidence that more than one type of carbonation product is formed.

Carbonation appears to be accompanied by a decrease in the amount of non-evaporable water in the paste. Changes produced by carbonation do not appear to affect the rate of hydration, at least at later ages. Until recently, carbonation shrinkage was usually attributed to water released as the product of the reaction between CO_2 and hydroxides or hydrates. An hypothesis for the mechanism of carbonation shrinkage based on " dissolution of calcium hydroxide crystals while the crystals are under pressure " has been advanced by Powers.(10) Concurrent studies would indicate, however, that less than one mole of water is released per mole of reacted CO_2 even at early stages of the reaction(9); this suggests that other mechanisms may also be involved.

The present paper describes an exploratory study of the role played by carbonation in the dimensional changes of Portland cement products. It was designed to reveal general relationships, particularly where disagreement exists and where information is lacking. It is intended as a basis for subsequent detailed studies.

More specifically, it was desired to obtain equilibrium weight and volume changes over the full range of relative humidity, 100 to 0%, for three main conditions: drying in CO_2-free air; drying with subsequent carbonation; and drying with simultaneous carbonation. To obtain maximum effects, highly permeable mortars were compared with dense mortars and only 100% CO_2 was used for carbonation. Subsequent treatments of drying, re-wetting, and re-drying were designed to reveal relationships between the characteristics of the cement paste subjected to the above conditions.

Materials and methods

Two mortars were made with a perlite aggregate and two with natural sand (see Table 1); cement paste was used as a partial reference; and all mixes were made with the same ordinary Portland cement.

Each of the five batches was placed by hand in a 3×4×16 in. mould. After storage in a fog room, the prisms were demoulded and cured in fog at 73°F to the age of 21 days. They were then stored under water for 7 days, during which period they were cut by diamond saw while wet, to reduce the danger of pre-carbonation. Each prism was cut in half and each end ground to a plane surface into bars 3×4×5 in. The latter were cut lengthwise into the final test specimens of three sizes: $\frac{1}{2}\times\frac{1}{4}\times5$, $\frac{1}{2}\times\frac{3}{8}\times5$, and $\frac{1}{2}\times\frac{1}{2}\times5$ in. Triplicate specimens for each test condition were selected from the top, middle and bottom of each bar.

TABLE 1: **Composition of mortars and paste.**

Mix	Aggregate	Proportions	*w/c**
1	perlite	1:2 by volume 1:0·273 by weight	0·686
2		1:4 by volume 1:0·547 by weight	1·025
3	natural sand	1:2 by weight	0·399
4		1:4 by weight	0·678
5	—	paste	0·500

*includes water in aggregate

The larger cross-section was chosen for the main tests, partly for ease in handling and partly because of the success of other investigators with even larger specimens. A range of permeability and compressibility was achieved by the two mix proportions and the two aggregates.

All conditioning was carried out in large vacuum-type desiccators, the samples being arranged vertically over the respective relative humidity conditioners. Distilled water was used for 100% R.H., and anhydrous magnesium perchlorate and vacuum for 0% R.H. The 75, 50, 25 and 9% R.H. conditions were achieved by sulphuric acid solutions of suitable concentrations. CO_2-free air was obtained by injecting air filtered through an absorbent into the evacuated desiccator. Carbonation was effected by attaching a balloon filled with pure CO_2 to the evacuated desiccator.

A dial gauge extensometer was used to measure lengths to an accuracy of 0·0001 in. Change in length was calculated as a percentage of the original length before the start of conditioning. Weight changes to the oven-dry weight were measured to 0·001 g and calculated as percentage of " oven-dry weights " at 28 days. The latter were obtained by drying separate 28-day prisms for each of the four mixes at the start of each conditioning period. The drying was at 110–115°C to constant weight. From the losses in weight thus obtained, the " oven-dry weights " of the saturated prisms to be subjected to the different test conditions were then calculated. Although arbitrary, this was a convenient standard reference. Up to the end of the first stage, i.e. conditioning at each of the six relative humidities, all measurements were made in a room conditioned at 50% R.H. and 73°F. The very short exposure times affected weights and lengths very slightly. For the subsequent treatments of drying in vacuum over magnesium perchlorate, re-saturation, and final drying, all measurements were made in a "dry box" except for the saturated specimens.

Equilibrium was considered to have been reached when the average change in length did not exceed 0·002% and the average weight change did not exceed 0·2% over 14 days. In order to maintain a reasonably organized programme, however, it was not always possible to fulfil both requirements.

For the CO_2-free conditioning and for the drying with simultaneous carbonation, the average time to reach equilibrium for all relative humidity conditions was 100 days for the mortars and 140 days for the paste. Subsequent carbonation required an average of 65 days. The first drying over magnesium perchlorate in vacuum required 75 days, re-saturation 30 days, and final drying 45 days. Re-saturation consisted of soaking in water to constant weight. At the end of this period the prisms were, one at a time, surface-blotted to remove surface water and quickly weighed.

The amounts of CO_2 in the test specimens at the end of the last drying stage were determined by a standard method of direct chemical analysis. Hydrochloric acid was used for decomposition and an absorbent to collect the evolved gas.(11) Determinations were made in the CO_2-free samples as well, because some pre-carbonation had occurred in all samples during fabrication and curing. Corrections were made where necessary.

The cement paste specimens were only carried through the drying and carbonation stages before final drying, without the subsequent re-drying and saturation. The high concentration of CO_2 and the density of the paste evidently caused the development of stress gradients that resulted in early cracking of some of the more highly carbonated samples.

In addition to the standard 28-day samples, some were cured for 3 months and subjected to the same conditions. This was also done for the smaller specimens to check the effect of size.

Results and discussion

EQUILIBRIUM SHRINKAGE AND WEIGHT CHANGES IN FIRST STAGE

Values of equilibrium shrinkage for the four mortars cured for 28 days are plotted in Figure 1. The corresponding weight changes for mortars 1 and 3 are plotted in Figure 2; the others, including the paste, are similar in form. The individual data are too voluminous to be recorded in this paper.

Curves A are those for CO_2-free drying, curves B for drying with subsequent carbonation, and curves C for drying with simultaneous carbonation. It is important to recognize that curves B and C are different from the normal isotherm type.(4) In these experiments each point represents the average equilibrium value on triplicate specimens dried and/or carbonated from the original starting condition. The curves do not represent reversible states corresponding to changing conditions from high to low relative humidity.

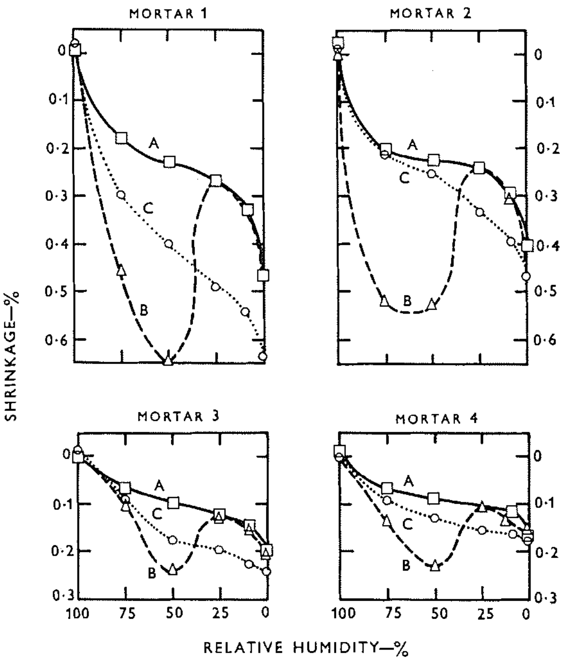

Figure 1: Relations between equilibrium shrinkage and relative humidity for mortars. A = drying in CO_2-free air ; B = drying with subsequent carbonation; C = drying with simultaneous carbonation.

CO_2-free drying

Curves A in Figure 1 are similar to the desorption isotherms obtained for Portland cement paste and other porous materials that have a common characteristic of shrinking progressively as they lose evaporable water. Another way of expressing this result is shown in Figure 4 where the shrinkage is plotted against moisture content. This curve shows clearly the three regions M-N, N-O and O-P which have been described and explained.(12)

In comparing the curves A in Figure 1, it may be noted that the slopes are influenced by the compressibility of the material, which, in turn, depends on the nature of the aggregate, the water/cement ratio, and the cement content. The apparent expansion at 100% R.H. is, of course, due to the arbitrary starting point.

The changes in weight in CO_2-free drying follow the normal pattern (see curves A in Figure 2).

Drying with subsequent carbonation

In Figure 1, curves B for this system show that the greatest total shrinkage (drying to equilibrium followed by carbonation to equilibrium) occurs between 75 and 50% R.H., with the maximum at about 50% R.H. At 25% R.H. the total shrinkage is essentially the same as for water-loss shrinkage, indicating

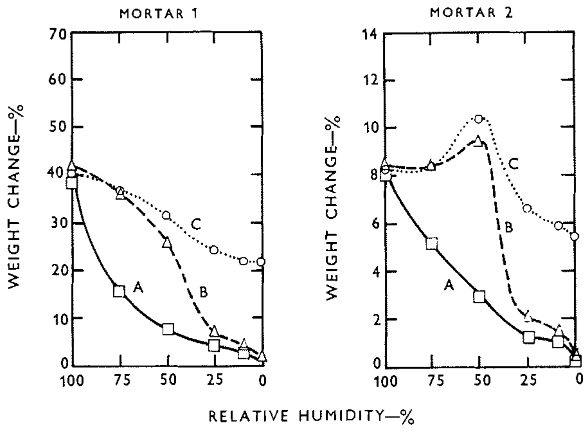

Figure 2: Relations between equilibrium weight change and relative humidity for mortars 1 and 3. A = drying in CO_2-free air; B = drying with subsequent carbonation; C = drying with simultaneous carbonation.

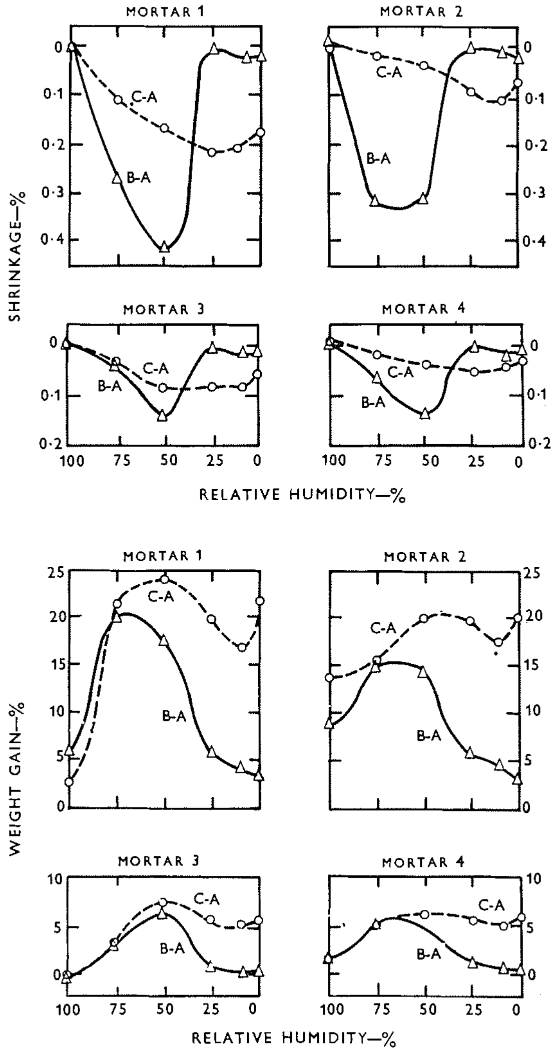

Figure 3: Equilibrium shrinkage and weight gain due to carbonation only. B – A = after drying; C – A = simultaneous with drying.

that no carbonation shrinkage has occurred. This agrees with Verbeck's findings(5), but it is contrary to results obtained by Alexander and Wardlaw(8). Below 25% R.H., the tendency for curves A and B to diverge slightly was at first attributed to experimental error, but this apparent anomaly (tendency to some shrinkage below 25% R.H. as against no shrinkage at 25% R.H.) occurred repeatedly throughout changes in weight and volume in the subsequent stages of treatment as well. In any event, the zero or nearly zero carbonation shrinkage from 25 to 0% R.H. is contrary to the results of Alexander and Wardlaw; Verbeck did not report for this range.

It may be noted that the maximum shrinkage due to carbonation alone was nearly double that of the water-loss shrinkage in mortar 1, and that it was about one-and-a-half times as great in the other three mortars; for the paste it was twice as great. These differences can be attributed to the differences in compressibility of the materials as they are influenced by type of aggregate, water/cement ratio and cement content.

In Figure 2 the curves of weight change for drying with subsequent carbonation (B) show a maximum divergence from those for CO_2-free drying (A) in the range of 75 to 50% R.H.

Figure 3 shows more clearly the actual shrinkages and weight gains due to carbonation alone. The points represent the difference between the values given in curves A and B. For carbonation after drying (B-A) the maximum carbonation shrinkage occurred at 50% R.H. for all mixes except mortar 2, the most porous material, where the maximum occurred at about 62% R.H. The very high compressibility of this material may have been responsible for the shift.

The net weight gains from carbonation alone, also shown as B-A curves in the lower part of Figure 3, yield maxima at 70, 65, 50 and 63% R.H. in order of mix number. In the paste samples, the maximum occurred at 50% R.H. However, two of the triplicate paste specimens cracked, owing to the stress gradients developed for this low-porosity material.

Thus, generally, the maximum carbonation increases with increasing permeability. It may therefore be concluded that when CO_2 can penetrate freely, maximum weight gains due to carbonation occur at a higher relative humidity (or moisture content) than the maximum carbonation shrinkage. Figure 3 also shows that considerable carbonation occurred at 100% R.H. for the porous mortar 2, but this decreased to practically zero for the low-porosity mortar 3. Some carbonation occurred between 25 and 0% R.H.

In this system it would appear that carbonation proceeds more rapidly and extensively at about 75% R.H. than at 50% R.H., possibly because more solution is present to facilitate reaction or because of a difference in the product of the reaction. At 50% R.H., however, it would appear that the greater tension in the capillary water, with resulting higher forces in the material, produces a greater shrinkage per unit of carbonation product. Evidently the carbonation product at 100%, at 25%, and at lower relative humidities is not conducive to shrinkage.

Drying with simultaneous carbonation

In Figure 1, curves C for this condition show an increasing divergence from curves A (CO_2-free) as the relative humidity decreases to about 25%. Because carbonation is accompanied by a release of water for at least a major part of the reaction and because time is required to extract water by drying, it is evident that the internal relative humidity of the sample will, at any given time, be higher than the ambient relative humidity. This accounts for the fact that maximum carbonation shrinkage occurs at about 25% R.H. (ambient) rather than at 50% R.H. as it does for subsequent carbonation.

In Figure 3 it may be noted that the maximum carbonation shrinkage due to simultaneous drying and carbonation (C-A) is about one-half to one-third of that resulting from drying with subsequent carbonation (B-A). Evidently, carbonation of the paste at very high humidities, possibly as high as 90%, confers some degree of volume stability that is retained throughout the lower humidity levels. It would appear that the more sensitive paste characteristics that obtain at 50% R.H. are not achieved in this system.

Below ambient 25% R.H., carbonation shrinkage decreases progressively as the internal relative humidity approaches the " insensitive " condition at 25% R.H.

The changes in weight for simultaneous drying and carbonation, as illustrated by curves C in Figure 2, also show a divergence from curves A (CO_2-free), but the maximum is at about 50% R.H. With the same reasoning as before, this maximum would correspond to some higher internal relative humidity, in all probability to the maximum of about 75% found in drying with subsequent carbonation. There is, therefore, an agreement in behaviour for both methods of carbonation as to both shrinkage and weight gain maxima.

Figure 3 shows that the extent of carbonation at the maxima is, in general, greater for simultaneous drying and carbonation than for carbonation after drying. This suggests that more extensive reaction occurs at the higher relative humidities, or that a different product is formed. The increase in carbonation below 25% R.H. is an apparent anomaly, as for the shrinkage referred to previously.

The paste samples subjected to drying with simultaneous carbonation behaved similarly to the mortars. But the three specimens conditioned at 50% R.H. cracked at 19 days; this was evidently due to the development of a high stress differential due to very rapid carbonation at the surface under these conditions.

RESPONSE OF SPECIMENS TO SUBSEQUENT DRYING AND WETTING

It was of interest to observe the effect of subjecting specimens that had reached the equilibrium states described above to three successive treatments: drying in vacuum over magnesium perchlorate, re-saturation, and drying again. The two stages of drying were intended to remove evaporable water.

These treatments were not designed to simulate normal cycling, but rather to reveal differences in response of those specimens that had presumably reached different levels of compressive stress. Volume stability conferred by cycling is considered as well-established(2,5) and was not a part of the study.

After CO_2-free conditioning

The results of this stage of the work have not been included in this paper because of shortage of space. It should be pointed out, however, that samples conditioned and stored at about 50% R.H. showed a different physical response to subsequent changes in conditions from that of samples conditioned and stored at other levels of relative humidity. It follows that samples conditioned near 50% R.H. should have a different sensitivity to volume change if some secondary reaction is involved, or where external load is applied as in creep. Powers has referred to this at various times.(10) This region of highest sensitivity may extend above or below 50% R.H.; the present data are too sparse to define the limits accurately.

An investigation reported by Hunt, Tomes and Blaine brings out concepts consistent with the above findings.(13)

After drying and subsequent carbonation

The three steps of drying, re-saturation and final drying were also carried out on specimens previously subjected to drying and subsequent carbonation. The results for mortar 1 are given in Table 2. With the minor exceptions noted, the other three mortars showed the same behaviour. It is to be noted that the effect of the original relative humidity of conditioning enters into the following results mainly by virtue of its effect on the extent of carbonation. Nevertheless, some interesting trends can be observed.

On first drying, a maximum in total shrinkage occurs for samples previously carbonated at 50% R.H., with the 75% R.H. samples near the maximum (Table 2, column 2). Corresponding maxima in " net weight gain "* due to carbonation occurred for the 75% R.H. specimens, with 50% R.H. samples near this maximum (column 3). The condition for maximum car-

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*In the following, the term " net weight gain " is used because the net weight changes of the " oven-dry weight " are positive with respect to the original " oven-dry weights " on which they are based.

TABLE 2: **Changes in length and weight of specimens of mortar 1 after drying with subsequent carbonation.**

Original equilibrium R.H. (%) (100 days CO_2-free, 65 days carbonation)	After first drying (75 days)		After re-saturation (30 days)			After second drying (45 days)	
	Total shrinkage	" Net weight gain "	Total expansion	percentage decrease in expansion	percentage increase in weight gain	percentage decrease in total shrinkage	" Net weight gain "
				compared with CO_2-free			
100–100	0·47	6·3	0·50	1	3	3	4·6
100– 75	0·71	25·5	0·36	11	15	34	24·2
100– 50	0·78	19·2	0·31	25	9	20	17·1
100– 25	0·47	4·1	0·39	4	0	11	5·8
100– 9	0·47	2·3	0·40	4	—1	14	3·7
100– 0	0·48	1·6	0·42	—1	—1	14	2·7

NOTES: Drying in vacuum over anhydrous magnesium perchlorate. Shrinkage is expressed as a percentage of the original saturated condition (28-day curing). The gain in oven-dry weight is given as a percentage of the oven-dry weight after 28 days curing. Negative values indicate expansion or loss in weight.

bonation does not, therefore, correspond to the condition for maximum shrinkage.

On re-saturation, expansion was at a minimum for those specimens previously carbonated at 50% R.H. (column 4). This evidence of volume stability is shown as percentage decrease in expansion as compared with the CO_2-free condition (column 5). The actual values in order of mortar numbers were: 25, 35, 38 and 32%. The corresponding increase in weight gain on re-saturation (column 6) yields a maximum for the samples previously carbonated at 75% R.H. (in mortar 3 at 50% R.H.).

On final drying, the percentage decrease in total shrinkage, compared with the CO_2-free samples, yielded maxima for specimens previously carbonated at 75% R.H., the values for the mortars being, in order, 34, 48, 30 and 46%. This may be taken as an indirect measure of the improvement in volume stability conferred by carbonation.

In comparing columns 8 and 3, it may be noted that the " net weight gain " at the maximum is less at the final drying than at the first drying. This is in contrast to the small " net weight gains " for the samples previously conditioned at the higher and lower humidities. If the hydration gains with time are taken into account, this considerable net loss at the maxima may be attributed, at least in part, to continued reduction in chemically combined water.[(9)] It may also be a result of some change in the nature of the carbonation product; Kroone and Blakey found different degrees of stability in such products.[(7)]

It may be recalled that a mild controversy exists as to whether, on desorption, the last menisci disappear at 45% R.H.[(10)] or at 31% R.H.[(12)]. The indirect and presumptive evidence in the present study favours the latter. Plots of total shrinkage against weight loss for both drying with subsequent carbonation and drying with simultaneous carbonation yield two distinct curves with junctions nearer the 31% R.H. value (recall Figure 4).

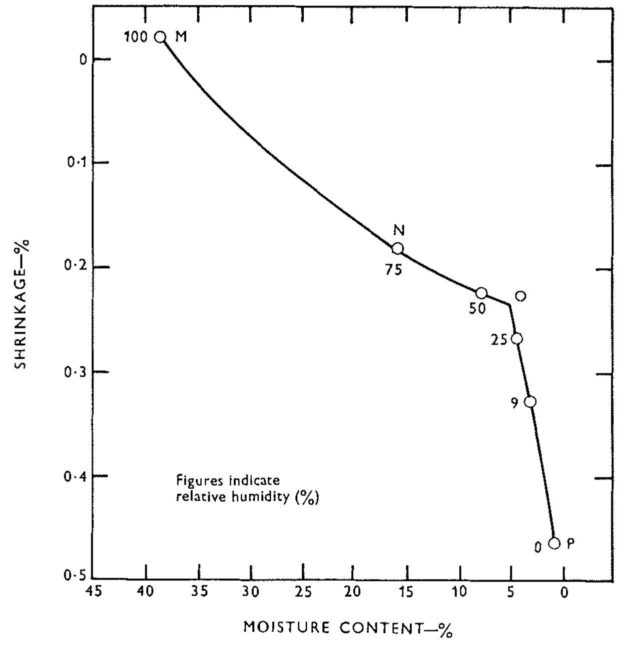

Figure 4: Equilibrium relations between shrinkage and moisture content under CO_2-free conditions for mortar 1.

After drying with simultaneous carbonation

Results for this conditioning are not reported; they yielded maxima and minima of shrinkage and weight gain corresponding closely to those above. In comparison with the results on the CO_2-free specimens, the percentage decrease in total shrinkage at the maxima was somewhat greater for simultaneous than for subsequent carbonation; this was also true for " net weight gain ". Since simultaneously dried and carbonated mortar contains more moisture during carbonation than pre-conditioned material, the optimum condition for maximum carbonation may be even higher than 75% R.H. or carbonate products at high humidities may be different from those at lower humidities. The results also showed that carbonation at the high humidities (during the early drying in this series) conferred considerable volume stability on the mortars.

In this series very extensive carbonation occurred at the 100% R.H. condition for mortar 2, the most permeable and open-textured material, and decreased with decreasing permeability. Apparent abnormalities in shrinkage and carbonation " net weight gain " for 25 to 0% R.H. were in evidence here also.

EXTENT OF CARBONATION

Direct CO_2 determinations by acid decomposition were made after the final drying stage on single specimens from each set of triplicates. This was done for mortars 1 and 2 and for the paste; the natural sand had too high a carbonate content to allow reasonable accuracy by difference.

The original CO_2 content of perlite aggregate was 0·12%; that of the cement, 0·72%. The CO_2 contents, as percentages of the cement content, for mortars 1 and 2 conditioned under CO_2-free conditions were 1·7 and 2·7% respectively; for the paste, it was 0·1% owing to pre-carbonation during fabrication and curing.

Table 3 compares the " CO_2 gains " that resulted from drying with subsequent carbonation with the corresponding " net weight gains ", each corrected for the corresponding CO_2-free condition. It may be noted that actual CO_2 gains for the 50 and 75% R.H. specimens are higher than the weight gains obtained from the equilibrium end-points and the differences in ignition loss. (The latter are the differences between the ignited weights of carbonated and uncarbonated samples of the same material at the same stage in conditioning.) This is not always true for specimens carbonated at 100% or at low relative humidities. One must take into account four factors that make for the differences noted:

water loss accompanying carbonation;

water gain through continued hydration with time;

decrease in non-evaporable water as a consequence of carbonation;

possible differences and changes in the nature of the carbonation products.

For the highly carbonated specimens (75 and 50% R.H.), the water loss accompanying carbonation has been greater than the water gain accompanying hydration. (The actual CO_2 contents are considerably higher than the weight gains at the three steps in conditioning shown in Table 3.) This is additional evidence that carbonation produces a net decrease in the amount of chemically combined water.(9,15) Below 25% R.H., where carbonation was low, it is evident that the small decrease in non-evaporable water is roughly of the same magnitude as the water gained through continued hydration with time.

Similar trends were observed for samples previously dried with simultaneous carbonation.

On the basis of CO_2 analysis on the single specimens described above, the extent of carbonation was calculated as a percentage of ultimate carbonation by the method used in other investigations.(10,14) Table 4 gives the results as total percentages of ultimate carbonation based on analyses of CO_2 and as gain percentages based on the " net weight gain ".

Considering the high permeabilities of mortars 1 and 2, the length of the carbonation period and the high concentration of CO_2, one would expect ultimate

TABLE 3: **Comparison of " net weight gains " with actual CO_2 gains for specimens of mortar 1 dried with subsequent carbonation.**

R.H. (%)	Gain after carbon-ation (%)	Gain after first drying (%)	Gain after second drying (%)	Difference on ignition at 1,050°C (%)	CO_2 gain by analysis (%)
100	5·9	3·5	3·6	3·2	5·3
75	20·0	23·9	23·4	22·3	27·0
50	17·6	19·2	15·1	15·1	21·0
25	3·2	3·2	4·4	3·7	3·3
9	1·7	1·6	2·8	2·3	1·4
0	0·8	0·4	1·6	1·6	0·5

NOTES: Each result from a single determination, corrected by subtracting corresponding value under CO_2-free condition. Gain in oven-dry weight expressed as a percentage of the oven-dry weight after 28 days curing.

TABLE 4: **Extent of carbonation of cement calculated on CO_2 contents: subsequent carbonation.**

R.H.	Carbonation as percentage of ultimate carbonation					
	mortar 1		mortar 2		paste	
(%)	total	gain	total	gain	total	gain
100	20	18	64	58	4	3
75	87	84	83	77	66	65
50	69	65	65	59	68	67
25	14	10	17	11	12	12
9	9	4	10	4	8	7
0	6	2	7	2	8	7

NOTES: Ultimate carbonation = 0·48 g CO_2 per g of cement.
" Total "—based on CO_2 analyses.
" Gain "—based on " net weight gain ".

carbonation to be nearer 100% than these calculations would indicate. Some doubt is therefore justified as to the assumptions on which calculations of ultimate carbonation have been based in the past.

The increasing carbonation at 100% R.H. with increasing permeability, or larger pore system, is again apparent. It is suggested that even at 100% R.H. the larger voids are not completely filled with water and that considerable diffusion of gas can occur. The fact that roughly 60% of ultimate carbonation occurs at 100% R.H., with no significant carbonation shrinkage, is not consistent with Verbeck's conclusion that the maximum should be in the order of 20%.(5)

It was possible to estimate the moles of water released per mole of CO_2 gained from the test data obtained. For highly carbonated samples (75 and 50%), the values ranged from 0·2 to 0·8 with an average of about 0·5. This is considered consistent with recent reports.(5,9)

MORTARS CURED FOR 28 DAYS AND FOR 3 MONTHS

In addition to the 28-day mortars, to which the foregoing results apply, some specimens were cured under water to the age of 3 months before being subjected to the CO_2-free conditioning and to drying with subsequent carbonation. Only the 50 and 9% R.H. conditions were compared.

For the dense sand mortars, shrinkages and weight gains due to carbonation were essentially the same: for mortar 3 the percentages of carbonation shrinkage were respectively 0·141 and 0·142% for 28-day and 3-month specimens at 50% R.H.; and 0·011% for 9% R.H. in both cases. The corresponding weight gains resulting from carbonation were, in order: 6·4 and 5·8% at 50% R.H. and 0·4% in both cases at 9% R.H. Similar agreement was obtained for mortar 4.

For the perlite mortars, however, the carbonation shrinkages at 50% R.H. were 23% higher for samples aged 3 months than for those aged 28 days, in spite of practically no difference in weight gain from carbonation. The same was true at 9% R.H. except that both carbonation shrinkage and weight gain were very low in each case.

These results indicate, then, that there is no increase in the extent of carbonation through prior ageing from 28 days to 3 months. On the other hand, a greater stress has apparently developed from the carbonation of the 3-month paste, so that although the dense sand mortar was not affected the perlite mortar suffered a considerably higher shrinkage. One hesitates to draw a conclusion here because several factors are involved: ageing produces more gel and hence a greater tendency to shrink; more gel decreases permeability so that penetration of carbon dioxide and loss of water is retarded; the perlite aggregate itself may suffer increased compressibility through longer soaking in the solution in the mortar; and the change in character of the paste induced by carbonation may be greater for the additional gel at 3 months.

The last possibility is tempting as a tentative explanation. It may be recalled that Verbeck's 7-day mortars subjected to drying with subsequent carbonation yielded carbonation shrinkage of the same order of magnitude as the water loss at 50% R.H.(5) In this study, the 28-day mortars (also with dense sand) yielded a corresponding carbonation shrinkage about one-and-a-half times as great as the drying shrinkage. The main difference in these mortars would appear to be the age at start of test.

It is interesting to compare the results of the 28-day and 3-month mortars in the CO_2-free system at 50 and 9% R.H. Ageing to 3 months produced the expected small increase in weight in all cases (additional hydration). In the dense sand mortars, the expected small decrease in drying shrinkage occurred. For the perlite mortars, however, there was an appreciable increase in shrinkage in the 3-month specimens over those cured for 28 days for both 50 and 9% R.H. conditions. The explanation may be that the additional hydration products in the more mature specimens provide additional stress after prolonged drying, but the effect appeared to be greater than can be accounted for by this difference.

RATES

Simultaneous drying and carbonation

Changes in volume and weight under this conditioning were measured periodically from 5 to 97 days at each relative humidity.

At 5 days only a very slight carbonation shrinkage had occurred for the 75 and 50% R.H. conditions; yet approximately 80% of the eventual total weight gain due to carbonation had taken place. As the internal humidities at this stage in drying would obviously be much higher than 75 and 50% R.H., probably over 95%, it is evident that at least a major part of carbonation can occur with no carbonation shrinkage, and that this can and does take place very readily at relative humidities only slightly below 100%. This would bear out early observations that carbonation can proceed extensively at very high humidities.(16) It would appear also that loss of water must occur for carbonation to produce shrinkage in such mortars.

After the initial rapid carbonation during the first 5 days (it occurred for small as well as large weight gains), further slow gains occurred at all humidities below 100%, even after carbonation shrinkage had reached a constant value. This would suggest that a secondary carbonation product is formed slowly, following the major reaction, and that it is not conducive to carbonation shrinkage. This secondary reaction may be topochemical in nature.(10) For the specimens dried at 0% R.H., carbonation shrinkage showed the usual gradual increase, but this was then followed by a slow decrease to a constant value. This would suggest that changes can occur in initial carbonation products with time.

Rates decreased, in order, as follows: 25, 9, 0, 50 and 75% R.H. for carbonation shrinkage; 50, 75, 25, 9 and 0% R.H. for carbonation. This is further evidence that the condition for maximum carbonation is at a higher relative humidity than the condition for maximum carbonation shrinkage.

Drying with subsequent carbonation

Changes in volume and weight were measured periodically from 12 to 68 days during the carbonation period.

At 12 days the 75% R.H. condition yielded the greatest weight gain and carbonation shrinkage relative to the final values. In the highly permeable mortar 2, the large initial weight gain was followed by a slow decrease, suggesting a change in the initial carbonation product with time.

At 100 and 25% R.H., the slight initial volume changes remained stable although, as expected, there was a slight but continuous weight gain due to carbonation. At 9% R.H., however, both weight gain and carbonation shrinkage continued to increase at a slow rate. At 0% R.H. the carbonation shrinkage also increased slowly, but initial weight gain decreased sharply with time. These apparent anomalies below 25% R.H. are again noted without explanation.

Drying under CO_2-free conditions

It is interesting that the rates of water loss and drying shrinkage under CO_2-free drying were decreased in order at relative humidities of 25, 9, 0, 50 and 75% (as for simultaneous drying and carbonation, see above). It is evident that these rates depend upon the rate at which the water is brought to the surface of the specimen as well as on the rate of evaporation. It would appear that the 25% R.H. condition provides the maximum gradient for the first process. Below 25% R.H. the drying plane recedes into the specimen and changes the character of the process.

SIZE OF SPECIMEN

As previously noted, the foregoing test results were based on $\frac{1}{2}\times\frac{1}{2}\times5$ in. specimens. The two smaller sizes, $\frac{3}{8}\times\frac{1}{2}\times5$ and $\frac{1}{4}\times\frac{1}{2}\times5$ in., were carried through the 50 and 9% R.H. conditions for the three series: CO_2-free drying, drying with subsequent carbonation, and drying with simultaneous carbonation. Comparison of final results indicated that, although differences had been considered negligible, the trend was definitely toward higher values for shrinkage and weight with decreasing size of specimen, even for the more permeable mortars. It is concluded that any refinements of such test values require thinner and highly permeable specimens.

Conclusions

Drying to equilibrium under CO_2-free conditions revealed that changes, apart from hydration effects, occurred in the mature cement paste, depending on the relative humidity. The greatest change occurred for the 50% R.H. condition where the results appeared to show a minimum in the non-evaporable water content, maxima in the total shrinkage and in " net weight gain " on re-saturation, and a maximum reduction in total shrinkage on final drying. These properties were associated with maximum sensitivity to secondary reactions and maximum stress due to capillary forces exerted by residual capillary water.

Subsequent carbonation of these specimens produced maximum carbonation shrinkage for those equilibrated at 50% R.H. In this case shrinkage due to carbonation ranged from one-and-a-half to two times that of water-loss shrinkage, depending on the compressibility of the material. Maximum carbonation, however, occurred for those specimens equilibrated at 75% R.H. Maximum carbonation shrinkage coincided also with a condition of apparently minimum non-evaporable water content, maximum capacity for water on re-saturation, and maximum reduction in total shrinkage on subsequent drying. No appreciable volume change due to carbonation occurred at 100% R.H. or between 25 and 0%, but there was some carbonation.

Drying with simultaneous carbonation under different relative humidities yielded higher maximum " net weight gain " but much lower maximum carbonation shrinkage than drying with subsequent carbonation. The most sensitive paste condition was therefore not achieved under this treatment. Early measurements for the 75% and lower relative humidities showed that most of the carbonation occurred while the internal relative humidity was still near 100%; there was no appreciable carbonation shrinkage, however, until lower internal humidity had been achieved later in the conditioning while the specimens were still exposed to CO_2. Thus, carbonation induces shrinkage only if the condition of the paste is at a moisture content corresponding to some relative humidity below 100%. In the highly permeable specimens very extensive carbonation occurred at 100% R.H. without carbonation shrinkage. Apparently anomalous weight and volume changes occurred at and below 25% R.H.

Early rapid carbonation, which requires the presence of water and an intermediate moisture content for maximum shrinkage, is followed by much slower carbonation at moderate and low humidities, the latter not accompanied by any significant shrinkage. There was evidence of change in the early carbonation products with time of drying.

It appeared that maximum or ultimate carbonation may be considerably less than the values previously accepted.

Curing from 28 days to 3 months did not increase the maximum extent of carbonation but the shrinkage stress appeared to become greater.

From a practical point of view, the extent of carbonation for a given concentration of CO_2 depends upon permeability, moisture content and time; the extent of carbonation shrinkage and ultimate volume stability depends upon compressibility of aggregate, water/cement ratio, maturity of paste, drying environment, and sequence of drying and carbonation. Simultaneous carbonation and drying at moderate relative humidities would appear to be the best condition for obtaining maximum volume stability.

Because carbonation can occur even at very high humidities, it would appear that dense concretes can, with time, suffer ultimate carbonation shrinkage at moderate humidities.

It is interesting to speculate on the significance of existing test data on shrinkage and creep. It is evident that test methods for these properties, involving long periods of time, must include means of eliminating or controlling carbonation. It is also interesting to speculate on the results of other tests on concretes and mortars subjected to conditioning in 50% R.H. environments stipulated by many specifications.

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