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Swenson, E. G.; Sereda, P. J.

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OTTAWA
April 1968

Price 10 cents

NRC 10096

MECANISME DU RETRAIT PAR CARBONATATION DE LA CHAUX ET DU CIMENT HYDRATES

SOMMAIRE

La carbonatation des éléments compactés de chaux hydratée produit un retrait et une modification des propriétés mécaniques de l'éprouvette comparables à ceux qui affectent les éléments traités de façon semblable de ciment hydraté en bouteille et les éprouvettes de ciment Portland durci. A l'aide des résultats expérimentaux obtenus par l'étude des systèmes plus simples à base de chaux, les auteurs formulent un mécanisme du retrait par carbonatation basé sur l'hypothèse d'une réaction par voie humide et l'établissement de cycles humidification-séchage.

Les expériences menées sur des éléments compacts de ciment hydratés en bouteille montrent que la chaux à l'état combiné est carbonatée au moins aussi rapidement et aussi complètement que la chaux libre, et que contrairement à l'opinion prévalente, les réactions affectant la première produisent un retrait de carbonatation plus grand que pour la seconde.
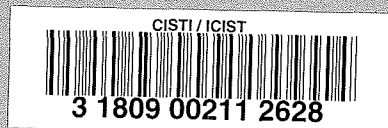
MECHANISM OF THE CARBONATATION SHRINKAGE OF LIME AND HYDRATED CEMENT

By E. G. SWENSON and P. J. SEREDA

Carbonatation of hydrated lime compacts produces shrinkage and changes in mechanical properties comparable with those found in similarly treated compacts of bottle-hydrated cement and samples of hardened Portland cement paste. From experimental results obtained with the simpler lime system a mechanism for carbonatation shrinkage is proposed that postulates a through-solution reaction and induced cycles of wetting and drying.

Experiments on compacts of bottle-hydrated cement show that carbonatation of the 'combined lime' is at least as rapid and extensive as the carbonatation of the 'free lime,' and that contrary to current opinion the former reaction results in even greater carbonatation shrinkage. The mechanism for carbonatation shrinkage of this system is considered to be connected with dehydration and polymerisation of the hydrous silica product of carbonatation.

Introduction

Under normal conditions calcium hydroxide liberated during hydration of Portland cement may, with time, undergo one or both of two changes: ageing and carbonatation. These processes can significantly affect the properties of the hardened cement paste because the free $Ca(OH)_2$ may constitute more than 20% of the system. This amount can be nearly half the quantity of calcium silicate hydrates in the matured paste.

Studies have already been carried out on the ageing of lime in compacted systems.[1] Observations of ageing and subsequent experiments on carbonatation of compacted lime powders have now led to new concepts regarding the carbonatation of lime and cement paste.

A compact of $Ca(OH)_2$ conditioned at an intermediate relative humidity, e.g. 50%, will undergo a small but irreversible shrinkage.[1] If such a compact is subjected to cycling between two relative humidities, e.g. between 50 and 75%, a net irreversible shrinkage will result after each cycle at both the upper and lower humidities. If such cycling occurs, for example, between 50 and 0% R.H., the drying shrinkage is of the same order of magnitude as the carbonatation shrinkage under 50% R.H. conditions. More important is the progressive, irreversible contraction at both upper and lower relative humidities, with the sample continuing to shrink with each successive cycle. This type of drying shrinkage, which may be considered to be a result of ageing, has not been generally recognised.

The mechanism of carbonatation shrinkage of lime is considered to be related to that of ageing of lime, i.e. a dissolution of strained material at areas of contact and re-deposition (precipitation) at sites of lesser stress in association with a cyclic change of humidity between two levels.[1] Adsorbed water and capillary water are the media through which the 'through-solution' reaction takes place. The new product is accommodated in the system and new linkages are formed.

To explain the results of the carbonatation experiments on lime the following tentative hypothesis is proposed.

The carbonatation reaction requires a specific minimum amount of water (condition of R.H.), and the rate of the reaction increases with increasing humidity but stops short of saturation; when the rate of reaction is high, a build-up of moisture occurs locally, representing a wetting half-cycle (water being a product of the carbonatation reaction); the carbonate product of the carbonatation reaction forms a relatively impervious coating on the lime, thus retarding the reaction and allowing the accumulated moisture to be removed by the ambient condition (this represents a drying

half-cycle); finally the drying shrinkage accompanying this last step results in cracking and opening up of the impervious coating, and this exposes the uncarbonated lime to further reaction and completes the cycle of wetting and drying.

The moisture trapped by the coating may be retained, but the moisture outside the coating will be removed by the ambient conditions; this would create a moisture content gradient in the coating sufficient to produce cracking. Shrinkage would not occur during the height of the carbonatation reaction because the particular locality would be saturated with the water product. The necessary sequence of deposition, slowing of the reaction, drying, and cracking would be out of phase at the different reaction points but the cumulative effect would correspond to a continuous process. In a rigid porous system the build-up of the coating product eventually stops the reaction and no further carbonatation takes place.

These postulates, when considered in relation to hardened cement paste, are at considerable variance with previous explanations.[2,3] They will be discussed in the light of the experimental evidence that follows.

Experimental

In this investigation the powder compact technique and associated methods developed in this laboratory[4] were employed. All compacts were made in a 1·25-in. dia. mould, and the compaction pressure is given as the total load in pounds applied to the piston.

Compacts of powdered lime were made from reagent grade calcium hydroxide (surface area (S.A.) = 7 m^2/g). Some were also made from calcium hydroxide powder produced by re-hydration in the vapour phase (at 25% R.H.) of the oxide, produced by calcining the reagent lime at 500° (S.A. = 12 m^2/g). The Type 1 cement used here was the same as that used in previous studies.[1,5]

Length change was measured by specially designed optical extensometers measuring to 0·000004 in. These, and the apparatus for measuring modulus, have been described elsewhere.[4,5] Knoop hardness was measured by a standard microhardness tester.

Extreme precautions were taken to prevent carbonatation during preparation of the sample in dry boxes and during preconditioning over sodium hydroxide solutions at controlled relative humidities.[1] In the latter case, the solution was stirred magnetically for a one minute period out of each 5 minutes to avoid friction heating, and the desiccators were fitted with flat 'Plexiglass' tops to permit readings to be taken of the optical extensometers.

Low concentrations of CO_2 were provided in the air in a 4-ft meteorological balloon. This gas–air mixture was conditioned to the desired relative humidity by bubbling through a sulphuric acid solution, and was then recirculated through the desiccator containing the samples by means of a fuel pump fitted with a flowmeter.

Pure CO_2 was supplied in a small balloon to the partially evacuated desiccators containing the samples and a solution of sulphuric acid to condition the space to the desired relative humidity.

Carbon dioxide contents were determined by decomposition with sulphuric acid, absorption of the evolved gas in barium hydroxide, and titrating with standard hydrochloric acid. A circulating closed system was used to provide high precision.

Results and discussion

Carbonatation of lime and hydrated cement

Samples in the form of discs or compacts were prepared to represent lime, bottle-hydrated cement and fully hydrated paste of 0·45 water/cement ratio. All samples were made to have equivalent 'coarse porosities' as determined by a 15,000 psi mercury porosimeter. Samples of these three systems, including sections mounted on optical extensometers, were preconditioned for 9 days at 50% R.H. and then carbonated with pure CO_2 under this humidity condition.

Fig. 1 shows that the rate and magnitude of carbonatation shrinkage of the compact of bottle-hydrated cement are very nearly the same as those of the hardened cement paste. In Table I similar close agreement is shown for modulus of elasticity and percentage carbonatation. In a previous publication[5] it was shown that the modulus of elasticity and the breaking strength were essentially the same for these two rigid porous systems, provided the porosities were the same. These studies further established the compact technique as a suitable method for investigating properties of hardened Portland cement paste.

Fig. 1 also shows that a compact of hydrated lime undergoes carbonatation shrinkage, despite the fact that the conversion of $Ca(OH)_2$ to $CaCO_3$ should theoretically result in an increase in unit cell volume whether the product be calcite, aragonite, or vaterite. This demonstrates directly that the carbonatation shrinkage of Portland cement paste is due, at least in part, to the carbonatation shrinkage of the lime constituent. Carbonatation shrinkage of the lime compact in a manner similar to that of cement paste is not compatible with a recent hypothesis that requires the dissolving of lime
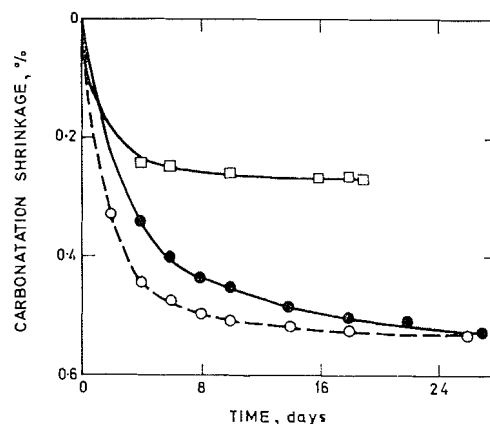

Fig. 1. *Carbonatation shrinkages of cement paste and compacts of hydrated cement and lime*
Approximately equal porosity
100% CO_2 at 50% R.H.
○ bottle-hydrated cement compacted at 70,000 lb   ● Cement paste, water/cement ratio 0·45   □ Calcium hydroxide compacted at 50,000 lb

crystals in a cement paste while they are under stress, the shrinkage then being considered to be a result of increased compressibility of the paste.[2]

In an experiment described later the greater carbonatation shrinkage of the paste specimens relative to that of the lime compact is shown to be connected with the carbonatation of combined lime as well as free lime. The difference in nature of the two materials is reflected in this property as well as in the modulus of elasticity (Table I).

Table I shows that, for a 'coarse porosity' of about 23%, the carbonatation is essentially stopped at about 50 to 60% of the theoretical value.

Carbonatation at varying relative humidities

Compacts of hydrated lime compacted at 20,000 lb were mounted on optical extensometers and preconditioned over NaOH solutions adjusted to provide relative humidities of approximately 25, 50, 75 and 95%. Upon reaching equilibrium (no further length change) they were transferred to desiccators containing H_2SO_4 solutions adjusted to provide the same relative humidities. They were then subjected to carbonatation with pure CO_2. Carbonatation shrinkage for each humidity condition is plotted in Fig. 2. Fig. 3 shows corresponding results on compacts of bottle-hydrated cement (60,000 lb).

TABLE I

Characteristics of cement paste and compacts of bottle-hydrated cement and lime before and after carbonatation at 50% R.H.

Sample	Before carbonatation			After carbonatation				
	CO_2, wt.-%	Porosity,* %	$E \times 10^{-6}$, lb/in²	CO_2, wt.-%	Percentage of total possible carbonatation	Porosity*, %	$E \times 10^{-6}$, lb/in²	Carbonatation shrinkage, %
Cement paste water/cement ratio, 0·45	3·1	23·9	1·8	24·1	60 (est'd)	12·1	2·7	0·525
Bottle-hydrated cement (70,000 lb) compact	3·2	23·2	2·0	20·9	50 (est'd)	11·0	3·1	0·551
Ca (OH)₂ (50,000 lb) compact	0·8	22·7	1·3	27·0	45	12·1	3·1	0·286

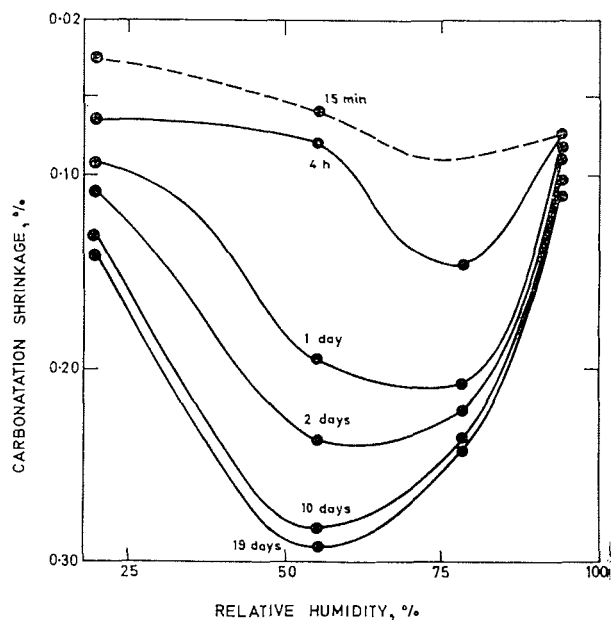*as determined by a 15,000 lb mercury porosimeter

Fig. 2. *Dimensional changes with carbonatation of 'aged lime' compacts*
Pre-conditioned for 14 days over NaOH solutions
Carbonated over H_2SO_4 solutions for 19 days
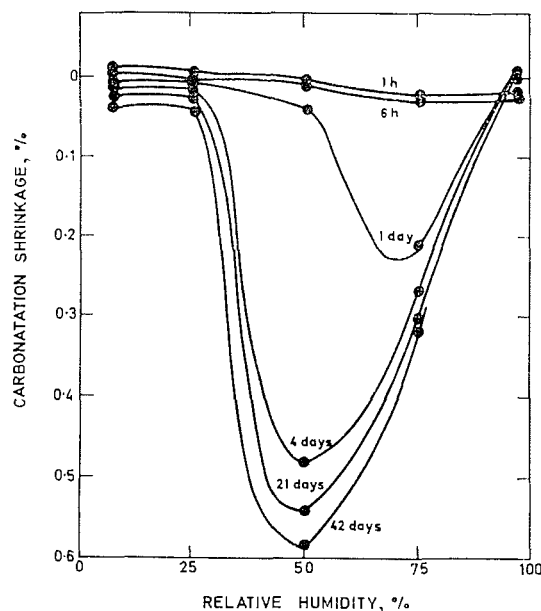Compaction load 20,000 lb
100% CO_2

Fig. 3. *Carbonatation shrinkage of bottle-hydrated cement compacts pre-conditioned at various relative humidities*
Compaction load 60,000 lb
100% CO_2

Both the lime and the bottle-hydrated cement compacts show a maximum carbonatation shrinkage at about 50% R.H. and relatively small carbonatation shrinkages at low and at high relative humidities (Figs. 2 and 3). Similar results have been obtained on cement paste specimens and on mortars in this and other laboratories.[3,6,7]

The curves of Figs. 2 and 3 are remarkably similar in form to the curves previously reported[1] for the ageing of lime. Other properties which exhibit maxima or minima at intermediate relative humidities are: surface area of Portland cement paste on storage,[8] and apparent thermal expansion of hardened Portland cement pastes.[9]

The degree of carbonatation, unlike the degree of carbonatation shrinkage, does now show a maximum, but increases with increasing relative humidity. In Fig. 2, the percent of total ultimate carbonatation after 19 days carbonation for the conditions of experiment shown were, going from low to high relative humidity: 13·7, 41·1, 48·0 and 77·9. In Fig. 3 the percent carbon dioxide by weight for the conditions of experiment shown were, from low to high relative humidity: 4·9, 8·0, 17·6, 18·0 and 21·8.

The similarity of the carbonatation shrinkage curves for lime and hydrated Portland cement is additional evidence that carbonatation shrinkage cannot be the result of increased compressibility of the paste arising from voids left by dissolved lime.[2] It is here proposed that the maximum carbonatation shrinkage is associated with the conditions that result in the maximum change in moisture content during the cycles of wetting and drying imposed by the four steps in the process described above.

The change in moisture content is influenced by the rate of the reaction (rate of production of water), ambient condition of R.H. (to establish the gradient of vapour pressure for drying), and the character of the material and its porosity (which determine the diffusion rates).[10] At intermediate

conditions of ambient R.H. there is a possibility of a large change in moisture content or R.H. during a cycle involving the four steps postulated in the above hypothesis and this should result in a large carbonatation shrinkage. At low ambient R.H. (10—25%) the reaction rate is very low. The removal of water from the reaction sites is therefore possible with little if any build-up of moisture and a correspondingly small change from the ambient condition; thus a small carbonatation shrinkage should result. At high ambient relative humidities, the rate of reaction is high but the water produced should cause little change in the high initial moisture content and only a small R.H. change. Thus, the proposed hypothesis explains the experimental results.

The hypothesis states that carbonatation shrinkage of lime in compacts is a succession of drying shrinkages resulting from the cycling phenomenon postulated above. It also states that the mechanism of shrinkage is similar to that occurring during ageing, i.e., a dissolution of the lime at points of contact and a redeposition of the product (lime in ageing, and calcium carbonate in carbonatation) at new points, producing new linkages. The consequence of dissolution of the original linkages, or bridges, is a shrinkage due to van der Waals forces, to menisci forces, to forces imposed by adsorbed water, or to any combination of these. Structurally, a new closer packing of particles results. The hypothesis denies that the relative humidity is directly responsible for the degree of carbonatation and carbonatation shrinkage.

Concentration of CO_2 and surface area of lime

Hydrated lime compacts made at a load of 20,000 lb were placed in extensometers, preconditioned at 50% R.H. and carbonated under this condition with CO_2 concentrations of 0·05, 1·0 and 100%. The curves for carbonatation shrinkage are shown in Fig. 4 and the final percentage carbonatation is given in each case.

The rate and degree of carbonatation shrinkage are not

much greater for a concentration of 100% CO_2 than for 1% CO_2. This indicates that the rate is governed by the diffusion process through the dense coating of the reaction products. Hence the CO_2 concentration difference of 100-fold does not influence significantly the rate of reaction. At the very low concentration of 0·05% the carbonatation shrinkage is much lower, indicating that the build-up of humidity is retarded and the range of the drying cycle reduced. Similar experiments were carried out at 95% R.H.: the carbonatation shrinkage for 1% CO_2 being 0·098% and for 100% CO_2, 0·110%—showing the same trend. The percentage of total possible carbonatation were, respectively, 81 and 78, as compared with the values for 50% R.H. shown in Fig. 4.

The low concentration of 0·05% CO_2 produced high gradients of carbonatation of a lime compact, depending on the orientation of the sample relative to the flow of the air/gas mixture. For this reason, most of the experiments were carried out at 1% CO_2 concentration.
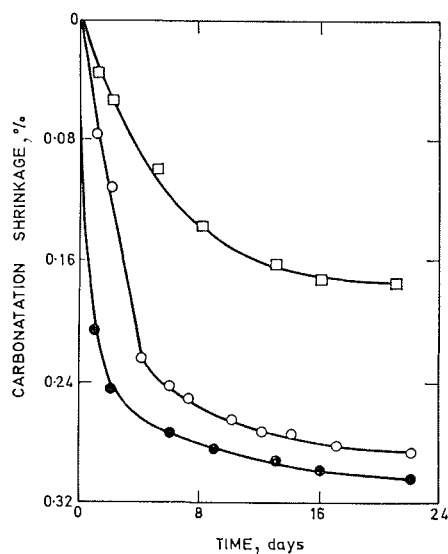

Fig. 4. *Effect of CO_2 concentration on carbonatation and carbonatation shrinkage of lime compacts at 50% R.H.*
20,000 lb compacts
□ 0·05% CO_2, 40% final carbonatation   ○ 1·0% CO_2, 43% final carbonatation   ● 100% CO_2, 41% final carbonatation

An increase in the length of the 50% R.H. preconditioning period from the usual 4 to 6 days to 3 weeks or more decreased carbonatation shrinkage by more than 50% but decreased the degree of carbonatation only very slightly. The preconditioning is an ageing process in which the sample undergoes some ageing shrinkage. The additional linkages produced will, on the basis of this hypothesis, provide for greater resistance to further internal rearrangement, denser packing and shrinkage.

Compacts were also made from lime obtained from vapour hydration of calcium oxide derived from igniting reagent grade $Ca(OH)_2$ at 500°. This product, having a somewhat greater surface area and having been produced by a different process, was compared with the reagent powder itself. The vapour hydrated lime can be assumed to have aged rapidly[1] during the hydration period; the surface area obtained exceeded that of the original powder by only 50% (Table II).

Preconditioning and carbonatation of the compacts

TABLE II

Influence of surface area on carbonatation and carbonatation shrinkage on lime compacts at 50% R.H.

Source of lime	Surface area, m²/g		Concn. CO_2	Carbonatation, %	Carbonatation shrinkage, %
	H_2O	N_2			
Reagent grade	12·6	9·9	0·05% 100%	40·3 41·4	0·175 0·300
Re-hydrated (vapour at 25% R.H.)	19·6	14·6	0·05% 100%	63·0 67·4	0·212 0·415

Compacts were made at 20,000 lb
Changes in mechanical properties of lime compacts due to carbonatation

mounted in extensometers were carried out at 50 and 95% R.H. The results of carbonatation shrinkage and degree of carbonatation are consistent with the initial surface areas of the limes (Table II).

A group of 20,000 lb lime compacts were preconditioned at 50% R.H. and another group at 95% R.H. After equilibration, they were carbonated at the same two relative humidities with 1% CO_2 in air. At intervals, determinations were made of percentage carbonatation, percentage carbonatation shrinkage, modulus of elasticity, and Knoop microhardness. The results are plotted in Figs. 5(a), (b) and (c).

Fig. 5(a) shows a somewhat greater increase of modulus with degree of carbonatation for the 95% R.H. condition than for the 50% R.H. condition. This might be expected because more solution is present in the former case and therefore, the product of carbonatation can be deposited more freely in small spaces where it can create new linkages, or 'bridges'.

Fig. 5(b) shows that microhardness describes a mechanical property for this system that parallels that of modulus of elasticity, giving curves with similar characteristics. Fig. 5(c) shows the higher shrinkage obtained when the carbonatation occurs at 50% R.H. as compared with the 95% R.H. condition. Table III records the final values of the above parameters and it is interesting to note that the 'coarse porosity' of the sample carbonated at 95% R.H. is only slightly less than that at 50% R.H. Much of the calcium carbonate product at 95% R.H. must have been deposited in finer pores.

These experiments demonstrate that carbonatation of lime compacts does not destroy their mechanical integrity even though there is a dissolution-deposition mechanism. On the contrary, these properties are improved. This is also true of hardened cement paste.[11] The above experiments also appear to show that the carbonatation products at 50 and 95% R.H. are not significantly different.

Effect of partial removal of free lime from hydrated cement

Much of the lime liberated during bottle hydration of lime with excess water is in the form of coarse crystals. These crystals can be largely removed by sieving. This technique was used to obtain products with different lime contents. Using another technique, the bottle-hydrated cement was dispersed in boiled distilled water and permitted to settle. The top layer was then separated from the coarser lower layer, which was richer in lime.
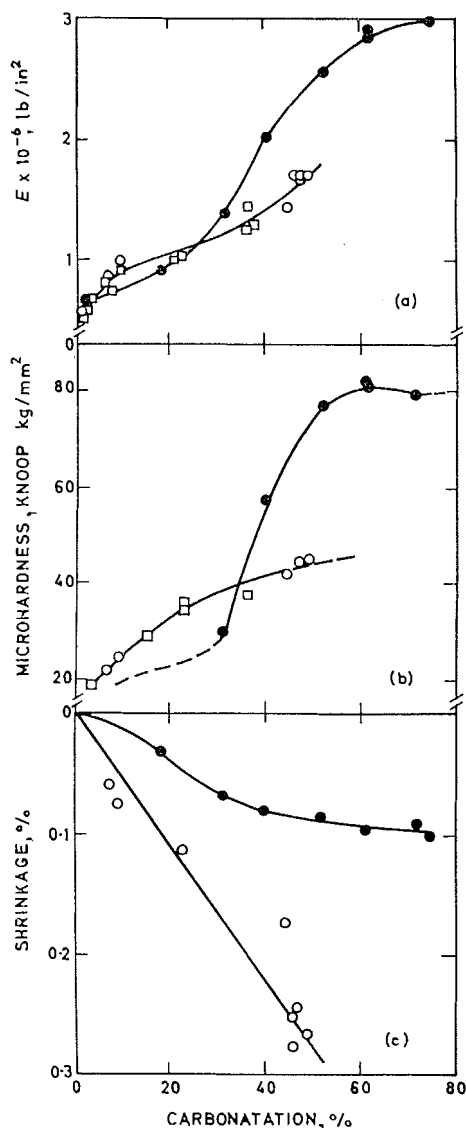
Fig. 5. *Changes in mechanical properties with carbonatation*
20,000 lb compacts
● Carbonatation at 95% R.H., 1% CO_2 ○ 50% R.H., 1% CO_2
□ 50% R.H., 0·05% CO_2

Fig. 6. *Effect of the change in lime content of bottle-hydrated cement on carbonatation and shrinkage*
20,000 lb compacts pre-conditioned at 50% R.H.
○ □ 1st series sieved samples   △ sieved plus water-extracted
● ■ 2nd series sieved samples   ▲ separation by sedimentation

The carbonatation shrinkages and CO_2 contents are plotted against molecular ratio of lime to silica in Figs 6(a) and 6(b).

Both carbonatation shrinkage and degree of carbonatation are shown to increase with decreasing free lime. The samples richest in free lime have carbonatation shrinkages approximating those of pure lime compacts. The samples lowest in free lime, and approaching the CaO to SiO_2 molecular ratio of 1·5, corresponding to tobermorite,[12] have shrinkages much higher than for compacts of bottle-hydrated cement. This result is noteworthy and not compatible with the generally held opinion that only the free lime is directly responsible for carbonatation shrinkage.

It should also be noted that degree of carbonatation also increases with decreasing free lime content. It appears that the rate and degree of carbonatation of the combined lime are at least as great as those of the free lime. These results do not agree with Powers' hypothesis that carbonatation shrinkage results from the dissolution and carbonatation of the free lime, leaving voids in the paste structure, and thus increasing compressibility.[2] They are also not compatible with his postulate that carbonatation of combined lime does not result in shrinkage.

All samples were compacted at the same load. This would result in some change in porosity as the proportion of lime was changed. The lower content of lime should give higher porosity; this could account for some of the higher carbonatation but could not account for the greatly increased shrinkage.

The major part of the free lime present in the bottle-hydrated cement is very coarse relative to the tobermorite-like material. The effect of this on rate and degree of carbonatation was not considered to be of significance as it had been found experimentally that the rate of carbonatation and shrinkage was about the same for compacts of bottle-hydrated cement as for cement paste normally hydrated.

TABLE III
Some properties of lime compacts after carbonatation

	Porosity, %*		After carbonatation			
R.H.,%	Before carbonatation	After carbonatation	$E \times 10^{-6}$, lb/in²	Carbonatation, %	Hardness, Knoop kg/mm²	Carbonatation shrinkage, %
50	34	29	1·7	47	45	0·29
95	34	25	3·0	82	81	0·10

*as measured by a 15,000 lb/in.² mercury porosimeter
Compacts were made at 20,000 lb

These products were analysed chemically for total silica and lime contents. Compacts were made of the powders at 20,000 lb load and these were mounted on optical extensometers. They were preconditioned at 50% R.H. and subsequently carbonated at the same humidity condition.
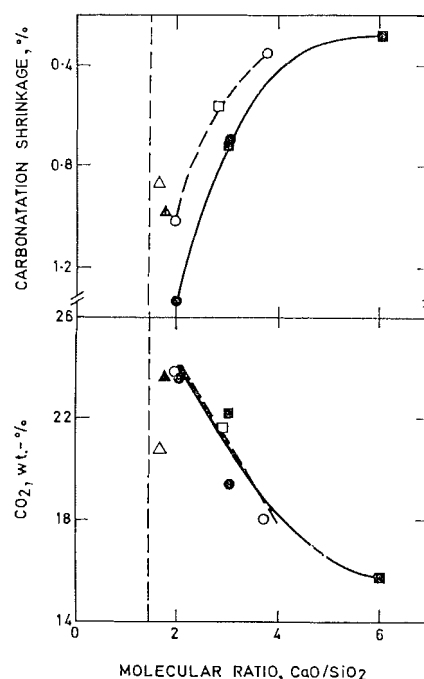
From the chemical analyses of the sample with low lime obtained by sedimentation, and presumably consisting mainly of tobermorite, it was calculated that over 80% of the calcium silicate hydrates had been decomposed by carbonatation. It is interesting that this apparent destruction of the main 'cementing constituent' of Portland cement paste does not impair the integrity of the solid structure. On the contrary, the carbonatation process results in a considerable increase in modulus of elasticity. These results must be considered in the light of concepts previously accepted without direct evidence: that the carbonatation of combined limes was very slow relative to the carbonatation of free lime and that the product of the reaction 'remains attached to the underlying silica and does not form a new phase of calcium carbonate'.[11]

The results of these experiments and those in Fig. 1 and Table I show that the free lime component of hardened Portland cement paste yields a lower carbonatation shrinkage than the calcium silicate hydrate component, and a lower percentage of ultimate carbonatation.

All experimental evidence supports the idea that the free lime in compacts or pastes of hydrated cement should involve the mechanism of carbonatation and shrinkage postulated for the pure lime compacts. It has been shown[13] that lime crystals in cement paste as well as bottle-hydrated cement have a distorted crystal lattice.

The same mechanism, however, cannot be postulated for the carbonatation of the combined lime. This involves a decomposition of the cement gel (tobermorite) and the formation of silica gels in addition to the calcium carbonate. These complex reactions may be also influenced by the hydrated products of C_3A and C_4AF.

The reported evidence is that silica gels tend to dehydrate gradually in an ageing process that results in a decrease in surface area.[14] 'The initially nearly liquid, mobile hydrogels produced by the decomposition of soluble silicates by dilute acids are continually changed by a systematic dehydration to a horn-like brittle substance like natural opal. A great part of the water in the initially jelly-like silicic acid may be 'squeezed out' of the inner framework of the colloid either spontaneously (syneresis) or by external pressures, etc.' Condensation (solidification) to polysilicic acids is brought about by foreign acids such as carbonic acid. It is probable that during carbonatation of calcium silicate hydrates there is, with time, a net release of water.

The gradual change from ageing colloids to crystalline aggregates is referred to as natural diagenesis, and is characterised by a marked increase in mechanical cohesion. This phenomenon is induced by mixed mineral hydrogels. For example, the precipitation optimum for $Al_2O_3.2SiO_2.2H_2O$ is provided if carbonates and free carbon dioxide are present.[14] It is thus probable that the mere presence of carbon dioxide and carbonate products has a catalytic effect on condensation of gel structures. Polymer formation in cement gel has already been shown to exist.[15] Such a reaction would have the net effect of providing for a shrinkage additional to the carbonatation shrinkage required by the hypothesis involving the lime constituent in the system.

More direct evidence for the above ideas is to be found in recent work by Lentz.[16] He noted that the formation of soluble polysilicates which normally increases with increasing hydration of cement paste, will decrease when the system is exposed to carbonatation. Lentz found that this resulted in an increase in the amount of insoluble polysilicate. He also noted that carbonatation tended to accentuate the decrease in orthosilicate and disilicate. Lentz was led to conclude that apparently carbon dioxide abstracts calcium ions from the calcium silicate hydrates, forcing continued polymerisation.

It would therefore appear probable that, as the carbonatation of hardened Portland cement paste occurs simultaneously on both the free lime and the combined lime in the calcium silicate hydrates, the resultant carbonatation shrinkage is due to two processes. One involves the shrinkage of the lime constituent by the mechanism already postulated, and the other involves a shrinkage resulting from dehydration and polymerisation of the hydrous silica product of carbonatation.

Summary and conclusions

Carbonatation shrinkage as well as rate and degree of carbonatation were found to be essentially the same for hardened cement paste and for compacts of bottle-hydrated cement, providing porosities were the same. Compacted lime produced similar relationships and was shown to be a significant system. Carbonatation shrinkage for the lime compacts was less.

For all three rigid porous systems, maximum carbonatation shrinkage occurred when samples had been preconditioned at 50% R.H. Much lower values were obtained at high and at low relative humidities. Degree of carbonatation, however, increased with increasing relative humidity.

Rate and degree of carbonatation and carbonatation shrinkage of lime compacts were essentially the same at 1% as at 100% concentration of carbon dioxide. Only at very low concentration (0·05%) was there a decrease in rate and degree.

Rate and degree of carbonatation and carbonatation shrinkage of lime compacts increased with fineness of lime. Mechanical properties of lime compacts were improved with carbonatation irrespective of preconditioning or of degree of carbonatation shrinkage. Degree of carbonatation of all three rigid porous systems was limited well below 100% of the theoretical value.

The results of these experiments led to a hypothesis for carbonatation and carbonatation shrinkage of lime compacts that should apply to the lime constituent in cement paste and compacts.

Carbonatation of lime, through solution, occurs most rapidly near contact points where the material is most strained and solubility is greatest. The calcium carbonate product would be deposited in spaces at and adjacent to the original contact points but with additional linkages. This is similar to the ageing process of lime.[1] Some shrinkage would occur as a direct result of this process if the relative humidity of preconditioning were conducive.

The largest part of carbonatation shrinkage of lime is postulated to be the consequence of cycles of induced drying shrinkage. This results from the following postulated four steps associated with carbonatation: that the reaction of lime and CO_2 begins at a minimum humidity of about 10% R.H. and increases with increasing humidity; that when the rate of reaction reaches a certain level, a build-up of water produced by the reaction occurs locally; that the solid product of carbonation forms an impervious coating on the lime; this retards the reaction and most of the accumulated moisture is then taken away by the ambient condition; that the drying involved in this last step should crack the coating and a new cycle will begin.

The maximum shrinkage resulting from the cycles of drying will depend upon the conditions that will allow the maximum

change in moisture content of both the lime and the carbonate formed during the reaction. It has been discussed how the intermediate condition of relative humidity should impose the largest change in the moisture content.

This irreversible carbonatation shrinkage, resulting from a rhythmic cycling, is not unlike the ageing shrinkage that occurs during cycling of lime compacts.[1] The rhythmic cycling is analagous to similar cycling occurring in certain precipitation and dissolution reactions.[14]

For compacts of bottle-hydrated cement, it was found that degree of carbonatation and carbonatation shrinkage increased as the amount of free lime present decreased. It is clear that carbonatation of combined lime also results in carbonatation shrinkage, to an even greater extent than for the free lime because the former is finer. The proposed hypothesis applies to the free lime component of this system but could not be expected to be applicable to the complex carbonatation reactions involving the combined lime where a decomposition of the silicate hydrate takes place. Carbonatation shrinkage in the latter system is considered to be connected with the dehydration and polymerisation of the hydrous silica product of carbonatation.

Acknowledgment

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