## 15 INFLUENCE OF MOISTURE ON CARBONATION SHRINKAGE KINETICS OF HYDRATED CEMENT PASTE

Y. F. HOUST
Laboratory for Building Materials, Federal Institute of Technology (EPFL),
Lausanne, Switzerland

Abstract
Small prisms of 3/3/90 mm were cut from large samples of hcp prepared with W/C from 0.3 to 0.8. After drying of the samples at constant rh ranging from 30 to 90% up to equilibrium lengths, $CO_2$ was introduced and its concentration kept constant at 2%. The length changes were measured as a function of time.
  It is shown that the kinetics of carbonation shrinkage of hcp can be well fitted by the hyperbolic function $\Delta l/l = $ at / b+t. The two parameters ("a" and "b") were calculated through the experimental measurements. The highest carbonation shrinkage reach 3 to 4 mm/m. The time necessary to get the half of the final shrinkage (the parameter b) is minimum between 50 and 80% rh for all hcp.
  After the shrinkage measurements, the $CO_2$ uptake of all specimens were determined. The relationship between the shrinkage and the $CO_2$ uptake is discussed with respect to the microstructure and the formation of minerals other than calcite.
Keywords: Hydrated Cement Paste, Carbonation Shrinkage, Microstructure, Carbonation Kinetics.

## 1 Introduction

The best known effect of carbonation on cementitious composites is the loss of alkalinity which protects the reinforcement against corrosion by passivation. Due to the carbonation, the pH of the pore water reduces to about 8. A less known effect of carbonation, hopefully with much less severe consequences, is carbonation shrinkage. The chemical reaction of carbonation leads to a reorganization of the microstructure, a decrease of porosity, and, paradoxically, a decrease in total volume involving a differential shrinkage between the surface and the bulk of the concrete which can lead to crazing. In its typical form, crazing is limited to the surface of the material and does not penetrate far into the mass. On structural elements, it can be distinguished from the major shrinkage cracks penetrating the entire mass which occur in concrete elements with restrained ends. Such cracks are due to drying shrinkage, Lea (1970).

## 2 Carbonation and carbonation shrinkage mechanisms

The carbonation of hcp is a chemical neutralization process of hydration cement products, i.e. essentially $Ca(OH)_2$ (calcium hydroxide) and C-S-H (calcium silicate hydrate) by carbon dioxide $CO_2$ present in the atmosphere at 0.03-0.04% by volume. The products of the carbonation of $Ca(OH)_2$ are $CaCO_3$ and $H_2O$ and those of C-S-H are $CaCO_3$, $SiO_2$ and $H_2O$. $Ca(OH)_2$ is essentially in crystal form and C-S-H is amorphous. $CaCO_3$ can
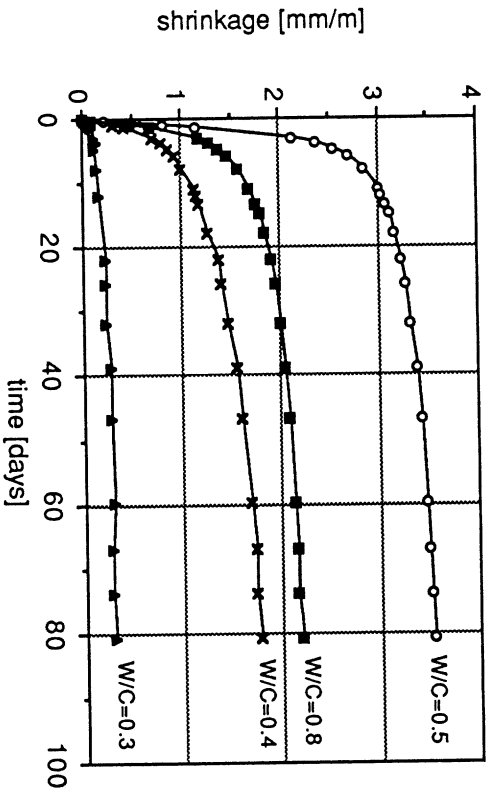
Fig. 2. Carbonation shrinkage of hcp exposed to 2% $CO_2$ (rh: 76%, temp.: 30°C).

The time to get the half of the final shrinkage (parameter b of equation 1) is minimum between 50 and 80% rh (fig. 3). It is also in this range that the rate of carbonation is maximum, Vénuat and Alexandre (1968). At high rh, the rate of carbonation shrinkage is therefore dependent of the rate of carbonation. At high rh, the rate of carbonation is controlled by $CO_2$ diffusion or by water diffusion out of the reaction zone. The role of water depends on the $CO_2$ concentration and on the porosity of hcp. Arliguié and Grandet (1991) have shown that an increase of the $CO_2$ concentration does not always induce an acceleration of the carbonation rate because the release of water blocks capillary pores, decreasing $CO_2$ diffusion. In our case, this effect is certainly important. Indeed, the influence of the rh on parameter b is much higher than that observed on the diffusion coefficient of $CO_2$, Houst (1992). At low rh, the pore water content allowing dissolution of Ca(OH)$_2$ is the limiting factor of carbonation rate.

After the carbonation shrinkage measurements, the prisms were crushed and their amounts of carbonate determined by means of an automatic carbon analyzer. This method is based on thermal decomposition of carbonate and subsequent quantitative determination using infrared $CO_2$ absorption. The results are presented graphically in fig. 4. It can be seen that the amount of carbonate (expressed as $CO_2$) increases with W/C for all rh, as the degree of hydration. It shows that it is essentially the hydration products which were carbonated. Parabolic curves were fitted to experimental results. The more porous the hcp, the more their maxima shift towards high rh. We could not find any.

Table 1. Parameters a [mm/m] and b [days] of equation 1 computed from curve fitting.

| rh [%] | W/C=0.3 | | W/C=0.4 | | W/C=0.5 | | W/C=0.8 | |
|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b |
| 90 | - | - | 0.76 | 117 | 1.60 | 135 | 1.77 | 58.0 |
| 76 | 0.31 | 9.73 | 1.95 | 5.86 | 3.85 | 3.10 | 2.00 | 2.97 |
| 48 | 2.07 | 12.0 | 1.63 | 13.4 | 1.52 | 13.3 | 1.45 | 9.64 |
| 30 | 5.09 | 312 | 2.38 | 66.1 | 2.62 | 54.3 | 3.70 | 70.5 |
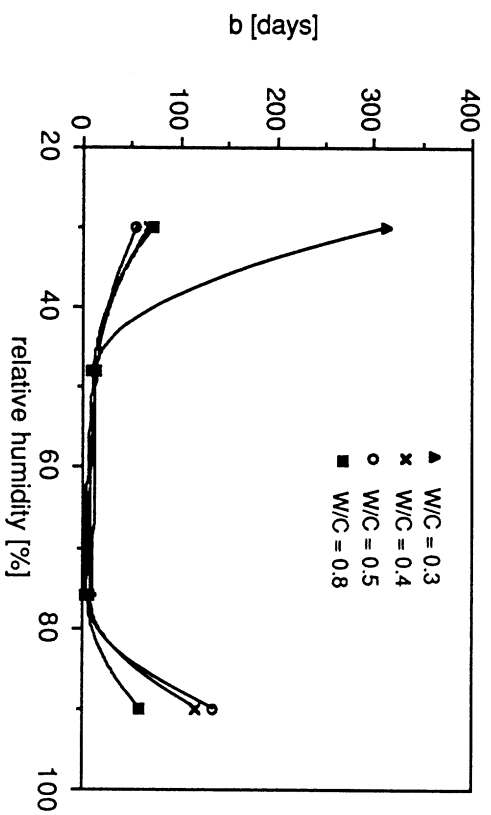
simple relationship between carbonation shrinkage and carbonate content, contrary to Alexander and Wardlaw (1959) who found a linear relationship between carbonation shrinkage and carbonation rate. It is possible that different crystal forms of carbonate can be formed, i.e. calcite, aragonite or vaterite. As already explained, the transformation of Ca(OH)$_2$ into CaCO$_3$ does not lead to the same augmentation in volume for the three mineralogical forms of CaCO$_3$. Nevertheless, the analysis of our specimens by FT IR always shows the presence of calcite only.
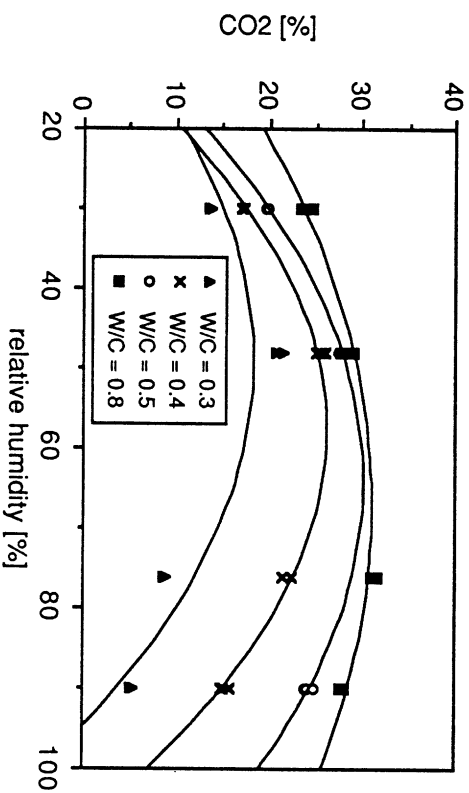


Fig. 3. Time necessary to reach the half of the final shrinkage (parameter b of equation 1).



Fig. 4. Carbonate content of hcp, expressed as $CO_2$, determined after exposing to 2% $CO_2$ and measurements of the carbonation shrinkage.

exist under three crystal forms. The transformation of Ca(OH)$_2$ into CaCO$_3$ causes an augmentation of volume depending on the crystal form, which is 3% for aragonite, 12% for calcite and 19% for vaterite. Calcite is the stable form under normal temperature and pressure, but the presence of the other two forms was reported as a product of carbonation. The augmentation of volume decreases the porosity of hcp.

Powers (1962) has proposed a hypothesis to explain carbonation shrinkage. He attributes this shrinkage to the solution of calcium hydroxide crystals which are under compression due to the drying shrinkage. Calcium carbonate is then formed in the pores free of stress. This can be only a partial explanation, because cement composites like autoclaved aerated concrete, which is practically free of calcium hydroxide, exhibits also large carbonation shrinkage, Houst and Wittmann (1989). Swenson and Sereda (1968) have suggested that carbonation promotes polymerization and dehydration of the C-S-H, leading to shrinkage. But none of these arguments can explain fully the mechanism of concrete carbonation shrinkage which is yet to be settled.

At rh higher than about 30%, the shrinkage due to simultaneous drying and carbonation is lower than that of the sum of drying shrinkage and subsequent carbonation shrinkage, Kamimura et al. (1965).

## 3 Experimental

### 3.1 Material

We prepared Portland cement paste cylinders of diameter 160 mm for various experiments on hcp as gas diffusion measurements, Houst (1990) and (1992). After at least six months of curing in lime water, prisms of 3 mm thick and 90 mm length were sawn from the large cylinders. As it is not possible to increase the water/cement ratio (W/C) of cement paste above 0.4 without having sedimentation and bleeding, it was necessary to keep cement particles in suspension before setting and hardening. Our ideas were based on previous work by Sereda and Swenson (1967) who prepared cement pastes with high water/cement ratios. It was necessary to bring some modifications because of the large diameter of our specimens compared to those of Sereda and Swenson (diam. 32 mm). Cement and water were mixed under vacuum and the cylindrical mold placed on a roller device for rotating the mix during setting and hardening, usually for a period of 48 to 72 hours. This method allowed us to prepare hcp with a W/C ratio from 0.3 to 0.8. The cement used was an ordinary Swiss Portland cement, corresponding approximately to ASTM type I.

Pore-size distribution, water sorption isotherms of non-carbonated and carbonated hcp, CO$_2$ diffusion through carbonated hcp as a function of the rh or water content were determined, Houst (1991) and Houst (1992).

### 3.2 Set-up - Procedure

After the sawing of the specimens, three prisms 3/3/90 mm were glued on the apexes of metallic triangles as shown in figure 1. A set of the three prisms forms a specimen stiff enough to allow us to measure the length changes. So one measured value is the mean value taken from three little prisms. The advantages of such little prisms are essentially the relatively short time to reach hygral equilibrium and then a large carbonation shrinkage. By assuming that these processes are governed by gas diffusion, it can be expected that their rate will be multiplied by four if the side of the prism is doubled.
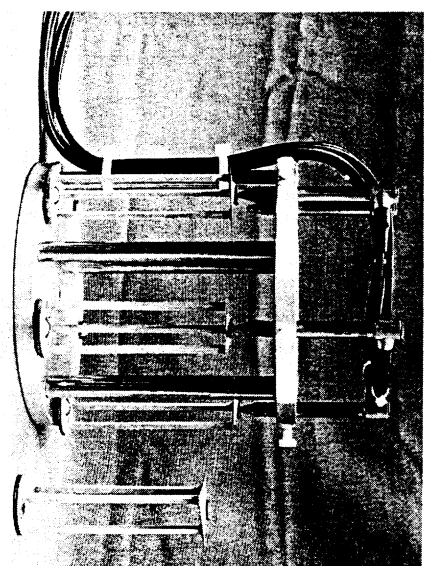
Fig. 1. Experimental set-up used for carbonation shrinkage measurements.

The specimens were set up into frames as the one shown in figure 1. The frames and the gauges were placed in an incubator with controlled relative humidity at 30°C. The shrinkage deformations were measured by taking length between two opposite metallic triangles. The deformations were measured with inductive gauges which had contacts made of a steel ball that fit into ring-shaped steel target glued on the upper metallic triangle which lays itself on a steel ball. Then, the length changes were recorded as a function of time. After drying at a constant rh up to equilibrium lengths, CO$_2$ was introduced and its concentration kept constant at 2% by volume. The carbonation shrinkage was then recorded during about 80 to 120 days, depending on the rate of shrinkage.

## 4. Results and discussion

The carbonation shrinkage of the hcp at 76% rh is shown in figure 2 as an example. Each point is the mean value of three measures taken from three different set-up. The following hyperbolic function has been fitted to experimental points:

$$\frac{\Delta l}{l} = \frac{at}{b+t} \qquad (1)$$

were $\Delta l/l$ is the carbonation shrinkage, t the time and a and b parameters. The parameter "a" is equal to the final shrinkage (t=∞) and "b" the time necessary to reach the half of the final shrinkage. These parameters computed for three other rh are reported in table 1. If one leaves the hcp with W/C=0.3 out of account, which has not a well defined behavior because of its very high compacity limiting strongly the diffusion of CO$_2$ and H$_2$O, the final shrinkage of the three other hcp seems to exhibit two maxima: one between 70 to 80% rh, the other at about 30% rh. Therefore, these results must be explained with caution. Essentially at low rh, the short-dated measurements, which appreciably stand aside the computed curve, have a too large weight in the fitting of the hyperbolic function. This is due to the lack of water necessary to the initiation of the chemical reactions.

Carbonation of the most porous hcp can reach 3 to 4 mm/m at relative humidities of 70 to 80%. These results are comparable to those obtained by Kamimura et al. (1965). But, their results were measured on mortars where shrinkage is restrained by the sand particles. Therefore, the carbonation shrinkage should be lower in mortars. As the size of their specimens were much larger than that of ours, it is possible that the mortars were not in hygral equilibrium and that the measured deformation was in fact the sum of a part of drying shrinkage and of carbonation shrinkage. Carbonation leads to a large modification of the microstructure and especially affects the C-S-H and causes release of water. The water sorption isotherms are strongly modified by carbonation and the equilibrium water amounts decrease appreciably at all rh after carbonation. The BET specific surface area is reduced to 50% by carbonation, Houst (1991) and Houst (1992). The loss of water induces shrinkage in a comparable way as to drying shrinkage. We explained our findings by the superposition of several phenomena: the carbonation reaction leads to the formation of calcium carbonate crystals of different sizes which oppose the shrinkage, water diffusion which promotes shrinkage, reorganization of the microstructure, of the capillary forces, of disjoining pressure, etc. These are certainly responsible for the phenomenon called carbonation shrinkage. But, we attribute the major role to the decrease of equilibrium water.

Young concrete surfaces are hopefully not often very porous and so in practice the rate of carbonation is low in a normal $CO_2$ concentration of 0.03-0.04%.

## 5 References

Alexander, K.M. and Wardlaw, J. (1959) A Possible Mechanism for Carbonation Shrinkage and Crazing, Based on Thin Layers of Hydrated Cement. **Austr. J. Appl. Sci.**, 10, 470-483.

Ariliguié, G. and Grandet, J. (1991) Représentativité des résultats d'essais accélérés de carbonatation sur éprouvettes de béton, in (**F. Auger Ed.**) **The Deterioration of Building Materials (Proceedings of the International Symposium)**, IUT, La Rochelle, pp. 245-253.

Houst, Y.F. (1991) Influence of Microstructure and Water on the Diffusion of $CO_2$ and $O_2$ through cement paste, in **Second CANMET/ACI International Conference on Durability of Concrete** (V.M. Malhotra Ed.), CANMET, Ottawa, Supplementary Papers pp. 141-159.

Houst, Y.F. (1992) **Diffusion de gaz, carbonatation et retrait de la pâte de ciment durcie** - Thèse EPFL No 1108, Ecole polytechnique fédérale de Lausanne, Switzerland.

Kamimura, K., Sereda, P.J. and Swenson, E.G. (1965) Changes in Weight and Dimensions in the Drying and Carbonation of Portland Cement Mortars. **Mag. Concr. Res.**, 17, 5-14.

Lea, F.M. (1970) **The Chemistry of Cement and Concrete** (2nd Ed.). Edward Arnold, London.

Powers, T.C. (1962) A Hypothesis on Carbonation Shrinkage. **J. P.C.A. R. & D. Lab.**, May, 40-50.

Sereda, P.J. and Swenson, E.G. (1967) Apparatus for Preparing Portland Cement Paste of High Water Cement Ratio. **Mater. Res. Stand.**, 7, 152-154.

Swenson, E.G. and Sereda, P.J. (1968) Mechanism of the Carbonation Shrinkage of Lime and Hydrated Cement. **J. Appl. Chem.**, 18, 111-117.

Vénuat, M. and Alexandre, J. (1968) De la carbonatation du béton. **Rev. Matér. Constr.**, No 638, 421-427.