

CARBONATION SHRINKAGE OF HYDRATED CEMENT PASTE

by Y. F. Houst

Synopsis: Large samples of hcp were prepared with W/C from 0.3 to 0.8 and small prisms of 3/3/90 mm were cut off . After drying the samples at constant rh ranging from 30 to 90% up to equilibrium lengths, CO₂ was introduced and its concentration kept constant at 2%. The length changes were recorded as a function of time.

It is shown that carbonation shrinkage of hcp can be well described by the hyperbolic function $\Delta l/l = at / b+t$. (where l is the length, t the time), a and b parameters).The highest carbonation shrinkage reaches 3 to 4 mm/m. The time necessary to reach half of the final shrinkage (the parameter b) is minimum between 50 and 80% rh for all hcp samples studied.

After the shrinkage measurements, all prisms were crushed and the CO₂ content, i.e. the CO₂ uptake of all specimens, was determined. The relationship between shrinkage and CO₂ uptake is discussed with respect to the microstructure and the formation of minerals other than calcite.

Keywords: Hydrated Cement Paste, Carbonation Shrinkage, Carbonates, Carbonation Kinetics.

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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 is reduced 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 in porosity, but, 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 bulk. On structural elements, crazing can be distinguished from major shrinkage cracks, which generally penetrates the entire mass and occur in concrete elements with restrained ends. According to Lea [1], such cracks are due to drying shrinkage. All these cracks can increase the rate of carbonation especially that of porous concrete.

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 carbonation products 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 exist in three crystal forms. The transformation of Ca(OH)_2 into CaCO_3 causes an increase in 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 also reported to arise to carbonation. The increase in volume decreases the porosity of hcp.

Powers [2] proposed a hypothesis to explain carbonation shrinkage where he attributed this shrinkage to the dissolution of calcium hydroxide crystals which are under compression due to the drying shrinkage leading to the

formation of stress-free calcium carbonate in the pores. This can only be a partial explanation, because cement composites like autoclaved aerated concrete, which is practically free of calcium hydroxide, also exhibits large carbonation shrinkage [3]. Swenson and Sereda [4] have suggested that carbonation promotes polymerization and dehydration of the C-S-H, leading to shrinkage. But none of these arguments can explain completely the mechanism related to concrete carbonation shrinkage and it is still to be settled.

Furthermore, it has been shown that, at relative humidity (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 [5].

EXPERIMENTAL

Material

Portland cement paste cylinders of diameter 160 mm were prepared for various experiments on hcp like gas diffusion measurements [6]. After at least six months of curing in lime water, prisms 3 mm thick and 90 mm long were sawn from large cylinders. As it is not possible to increase 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 [7] who prepared cement pastes with high water/cement ratios. It was however necessary to introduce certain modifications because of the large diameter of our specimens compared to those of Sereda and Swenson (diam. 32 mm). Cement and water were mixed in 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 W/C from 0.3 to 0.8. The cement used was a normal Swiss portland cement, similar to ASTM type I.

Physical properties like pore-size distribution, water sorption isotherms of non-carbonated and carbonated hcp, CO₂ diffusion through carbonated hcp as a function of the rh or water content were already published [6, 8].

Set-up - Procedure

Three prisms 3/3/90 mm were glued on the apexes of metallic triangles as shown in Fig. 1. A set of three prisms forms a specimen stiff enough to allow measurement of changes in length. Hence each measured represents the mean taken from three small prisms. The advantages of such small prisms are essentially the relatively short time to reach hygral equilibrium followed by a large carbonation shrinkage. By assuming that these processes are governed by

diffusion of gas, it can be expected that their rate will be multiplied by four if the side of the prism is doubled.

The specimens were set up into frames as the one shown in Fig. 1. The frames and the gauges were placed into an incubator with controlled relative humidity at 30°C. The drying shrinkage was measured by considering length between two opposite metallic triangles. The deformations were measured with inductive gauges which had contacts made of a steel ball that fit into a 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, CO₂ 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.

RESULTS AND DISCUSSION

The carbonation shrinkage of the different hcp at 76% rh is shown in Fig. 2,3,4,5. Each point is the mean value of three measurements taken from three different set-up. The following hyperbolic function was fitted to experimental points:

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

where $\Delta l/l$ is the carbonation shrinkage, t the time and a and b parameters. The parameter “ a ” is equal to the final shrinkage ($t=\infty$) and “ b ” the time necessary to reach the half of the final shrinkage. These parameters computed for four rh are reported in Table 1. If one leaves the hcp with $W/C=0.3$ out of account, which does not have a well defined behavior because of its very high compactness limiting strongly the diffusion of CO₂ and H₂O, 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 (Fig. 6). Therefore, these results must be explained with caution. Essentially at low rh, the short-term 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 initiate the chemical reactions.

The time to reach half of the final shrinkage (parameter b of equation 1) is minimum between 50 and 80% rh (Fig. 7). It is also in this range that the rate of carbonation is maximum [9]. The rate of carbonation shrinkage is therefore dependent on the rate of carbonation. At high rh, the rate of carbonation is controlled by CO₂ diffusion or by water diffusion out of the reaction zone. The

role of water depends on the CO₂ concentration and on the porosity of hcp. Arliguié and Grandet [10] have shown that an increase in the CO₂ concentration does not always induce accelerated carbonation because the released water blocks capillary pores, decreasing CO₂ diffusion. In our case, this effect is certainly important. Indeed, the influence of rh on parameter b is much higher than that observed on the diffusion coefficient of CO₂ [10]. 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 carbonate content determined by means of an automatic carbon analyzer. This method is based on thermal decomposition of carbonate and subsequent quantitative determination based on infrared CO₂ absorption. The results are shown in Fig. 8. It can be observed that the amount of carbonate (expressed as CO₂) increases with W/C for all rh, as the degree of hydration increases. 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 simple relationship between carbonation shrinkage and carbonate content, contrary to Alexander and Wardlaw [11] 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 CaCO₃ does not lead to the same increase in volume for the three mineralogical forms of CaCO₃. Nevertheless, the analysis of our specimens by FTIR always shows the presence of calcite only.

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. [5], who however measured carbonation shrinkage on mortars. Therefore, the carbonation shrinkage should be lower in mortars, since shrinkage is restrained by sand particles. As the size of their specimens were much larger than that of ours, it is possible that the mortars were not in hygral equilibrium before carbonation 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 [8]. The loss of water induces shrinkage in a comparable way as does drying shrinkage. These findings can be explained 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, the capillary forces, the disjoining pressure, etc. All these

causes are certainly responsible for the phenomenon called carbonation shrinkage. But, the major role can be attributed to the decrease of equilibrium water.

Carbonation shrinkage can increase the carbonation rate because of the formation of superficial cracks and so reduce the initiation period preceding the corrosion of the steel reinforcement. This effect is certainly more severe for highly porous cementitious materials

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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

Fig. 1 - Experimental set-up for carbonation shrinkage measurements

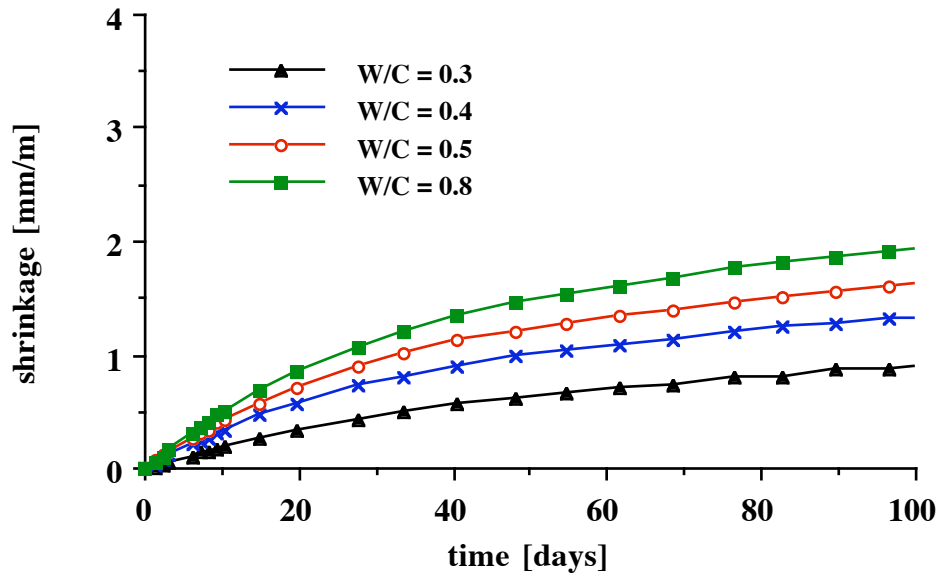


Fig. 2 - Carbonation shrinkage of hcp exposed to 2% CO₂ at 30% rh and 30 °C

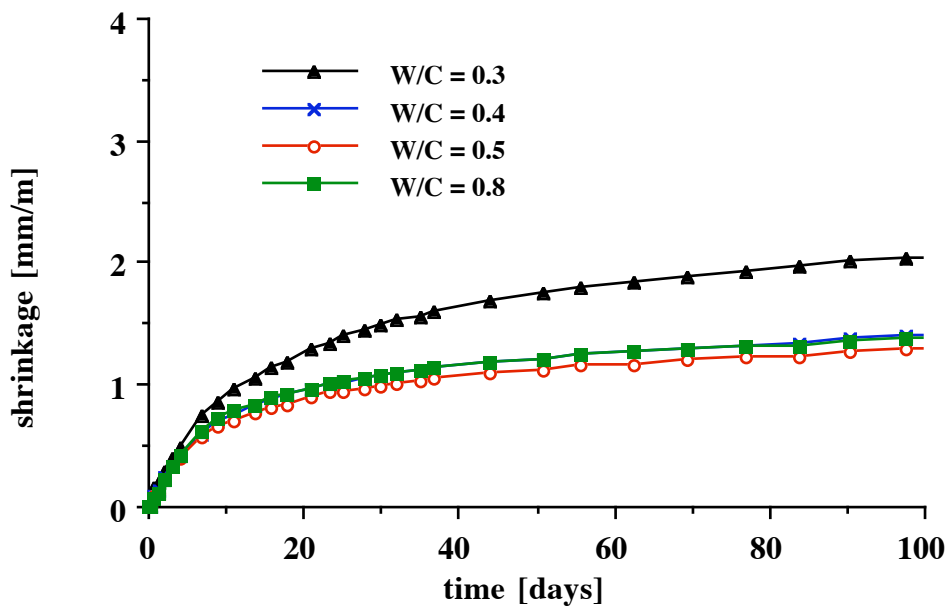


Fig. 3 - Carbonation shrinkage of hcp exposed to 2% CO₂ at 48% rh and 30 °C

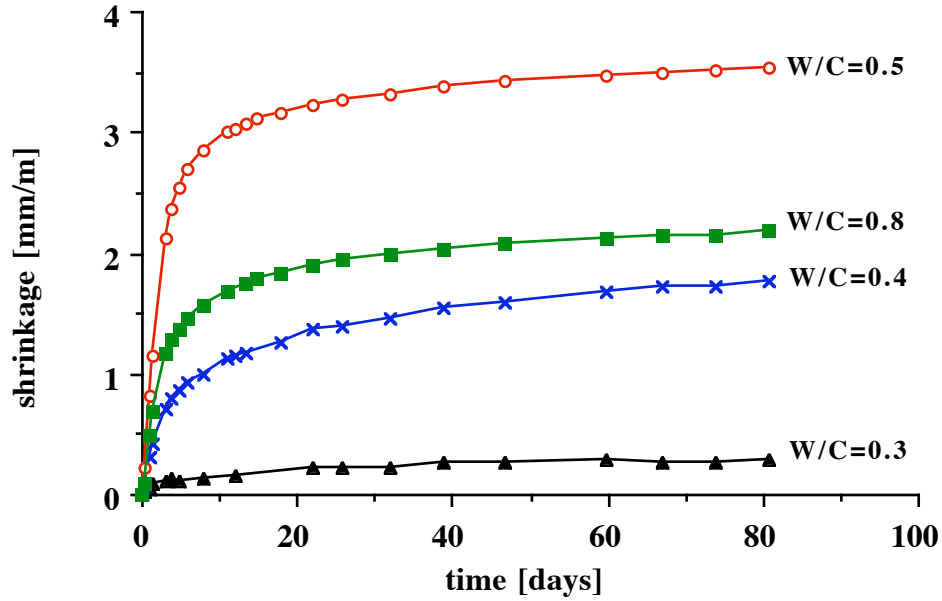


Fig. 4 - Carbonation shrinkage of hcp exposed to 2% CO₂ at 76% rh and 30 °C

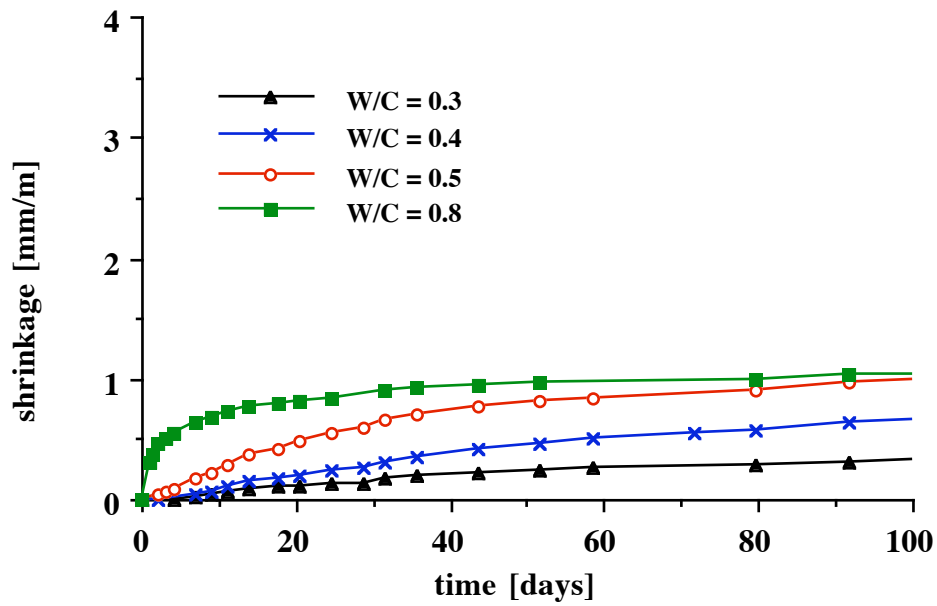


Fig. 5 - Carbonation shrinkage of hcp exposed to 2% CO₂ at 90% rh and 30 °C

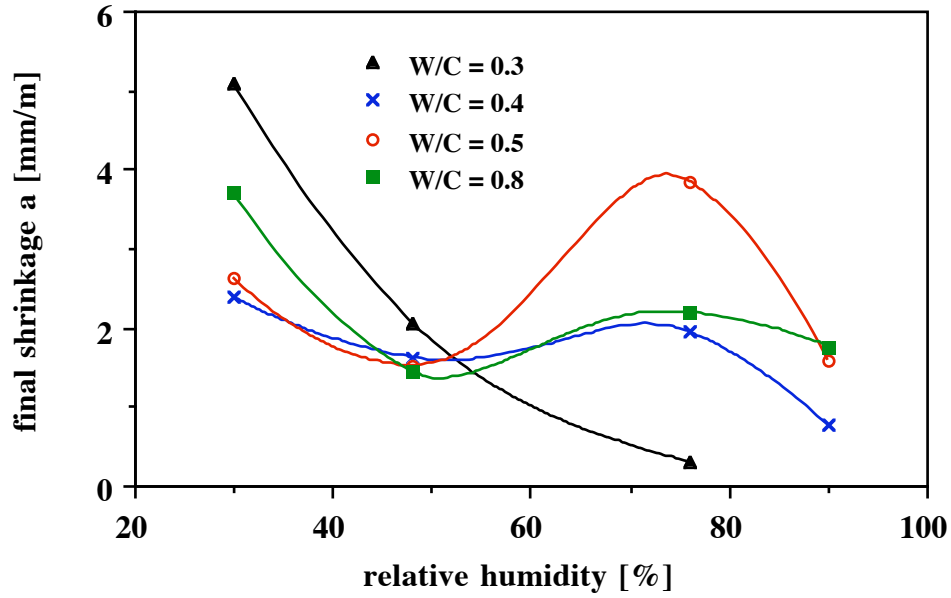


Fig. 6 - Time necessary to reach the final shrinkage (parameter “a” of equation 1)

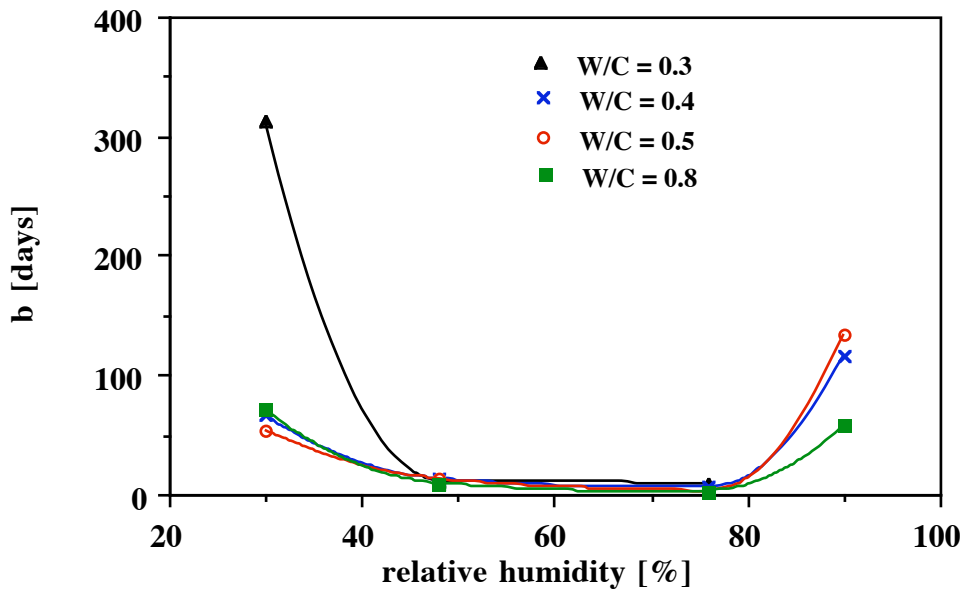


Fig. 7 - Time necessary to reach half of the final shrinkage (parameter “b” of equation 1)

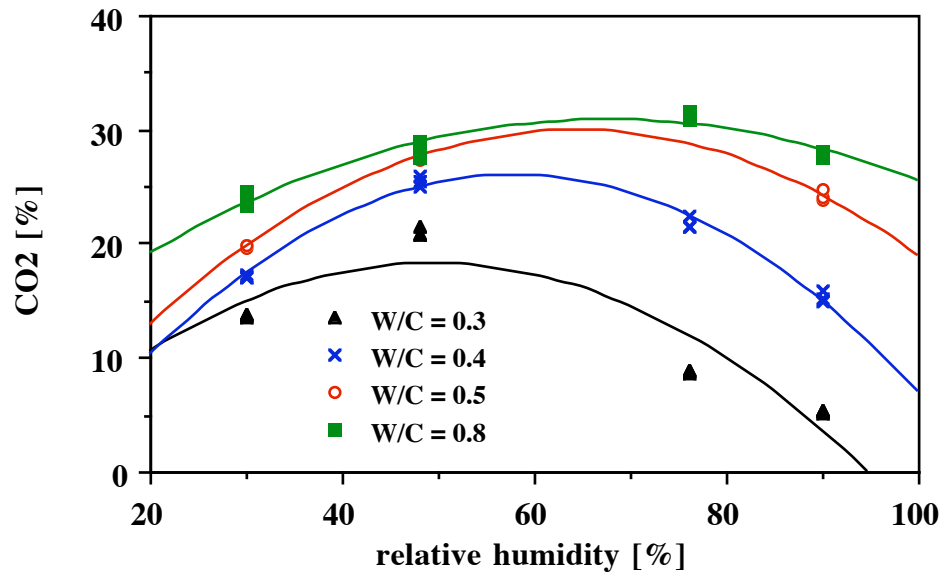


Fig. 8 - Carbonate content of hcp, expressed as CO₂, determined after exposure to 2% CO₂ and measurements of the carbonation shrinkage