

論文 Structure and Strength Development of Carbonated Mortar

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ABSTRACT: Change in mechanical properties, pore structure and phase composition of mortar due to carbonation was studied. The strength development of carbonated mortar is affected by change in phase composition as well as pore structure. Modulus of elasticity and stress-strain curve of carbonated mortar depend on type of cement, exposure condition and initial water curing. It was found that for blended cement mortar with high slag content, carbonation does not only hinder the strength development but also reduces the stiffness.

KEYWORDS: carbonation, compressive strength, modulus of elasticity, phase composition, pore structure, stress-strain curve.

1. INTRODUCTION

Carbonation of concrete is undesirable process due to its detrimental effect on reinforcing bars. However, it was reported that compressive strength of concrete made of ordinary portland cement increases with carbonation due to reducing of its porosity. Even application of rapid carbonation to portland cement mortar under high CO_2 concentration has been known to develop strength rapidly. But, it was also reported that compressive strength of concrete made of slag sulphate cement and of blast furnace cement is decreased by carbonation due to coarsening of the pore structure.

The present investigation was undertaken to study and correlate the reaction properties and mechanical properties of mortar made using OPC (Ordinary Portland Cement) or PBFSC (Portland Blast Furnace Slag Cement), after exposure to various concentration CO_2 .

2. EXPERIMENTAL WORKS

2.1 MATERIALS AND MIX PROPORTIONS

Cements used to prepare mortar cylinders were ordinary portland cement and blended cements (50% and 75% ground granulated blast-furnace slag by mass). Chemical composition of both the ordinary portland cement and the ground granulated blast-furnace slag are given in Table 1. Standard Toyoura sand was used as fine aggregate. Mortar with water-binder ratio of 0.6 were prepared. Mix proportions of mortar are given in Table 2.

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2.2 FABRICATION AND CURING

After casting, mortar cylinders of diameter 5 cm and height 10 cm were cured in moist room at 20°C for one day and then demolded. Subsequently, the cylinders were cured in water for 0 and 27 days. Afterwards, slices with about 2 mm thickness were taken out from the middle portion of specimen (about 3 cm from top and bottom surface). Then, specimens were conditioned in various environments (water, air with 0.07% CO₂, carbonation chambers with 1%, 10% CO₂ by volume and cyclic -one week in carbonation chamber with 10% CO₂ and one week in water-). In all cases the relative humidity of the ambient air was 60% at 20°C.

2.3 MEASUREMENT

After exposure, compressive strength and carbonation depth (phenolphthalein was used to distinguish carbonated portion from uncarbonated portion) were measured at the ages of 1, 4, 8, 12, 20, 28 and 52 weeks. Modulus of elasticity and stress-strain curve of specimens were also measured at the age of 52 weeks. Three cylinder specimens were used at each condition of exposure for compressive tests. And the values obtained for compressive strength and modulus of elasticity are the average values at each condition. Pore size distribution ($r > 3$ nm) of sliced mortar, measured by mercury porosimetry, were determined at the ages of 4, 12, 28 and 52 weeks. The reaction products of sliced mortar were also studied by differential thermal analysis (DTA).

3. RESULTS AND DISCUSSIONS

In the previous papers[1,2], the authors have reported how carbonation affects the development of compressive strength and pore structure of mortar until 28 weeks exposure period. Even, the relationship between compressive strength and pore structure of carbonated mortar has been presented[1]. In the present paper, the role of phase composition in development of compressive strength and how carbonation affects modulus of elasticity and stress-strain curve of carbonated mortar have been examined thoroughly.

3.1 PHASE COMPOSITION OF CARBONATED MORTAR AND ITS RELATION WITH COMPRESSIVE STRENGTH

(1) Ca(OH)₂ and CaCO₃ content

The DTA records of the OPC sliced mortar studied are shown in Figure 1. The samples were taken from sliced OPC mortar with 28 days initial water curing at 1 year exposure period. Since the thickness of sliced mortar is only about 2 mm, all of them which were exposed to air, 1%, 10% CO₂ and cyclic condition, have been completely carbonated at 1 year exposure period. An endothermic effect at about 475°C indicates the presence of Ca(OH)₂. Most of the

Table 1. Chemical compositions and physical characteristics of OPC and GGBFS

	Ordinary portland cement	Ground granulated blast-furnace slag
Ig. loss	1.2 %	---
Insol.	0.4 %	---
SiO ₂	21.9 %	34.3 %
Al ₂ O ₃	5.0 %	14.6 %
CaO	64.2 %	42.2 %
Fe ₂ O ₃	2.8 %	0.2 %
MgO	1.7 %	6.4 %
Specific weight	3.15	2.90
Specific surface area	3230 cm ² /g	4010 cm ² /g

Table 2. Mix proportions of mortar (60% W/C ratio)

% slag content	Cement	Water	Slag	Sand	Initial curing period
	(kg/m ³)				
0	598	359	----	1196	0 and 27 days
50	297	356	297	1187	
75	148	355	444	1178	

thermograms show two endothermic peaks beyond 700°C, which the endotherms at lower and higher temperature could be attributed to poorly-crystallized and well-crystallized CaCO₃ respectively. Miskovsky, J.[3] reported that humidity is the reason of the transformation of the poorly-crystallized CaCO₃ into well-crystallized, stable CaCO₃. Transformation and recrystallization of poorly-crystallized CaCO₃ was associated with strength decrease. The thermogram of mortar which was cured in water shows only an endothermic peak at about 700°C with lower intensity, showing the presence of CaCO₃. It can be noticed that Ca(OH)₂ was consumed by its reaction with atmospheric CO₂ to produce CaCO₃. The presence of Ca(OH)₂ in mortar exposed to air can still be noticed although it is not as much as the Ca(OH)₂ of mortar cured in water, while its content of well crystallized CaCO₃ is much lower than those of mortar exposed to high concentration of CO₂.

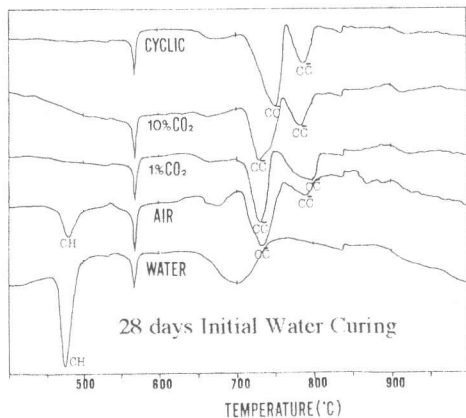


Figure 1. Thermograms of OPC mortar exposed to various environments for 1 year.

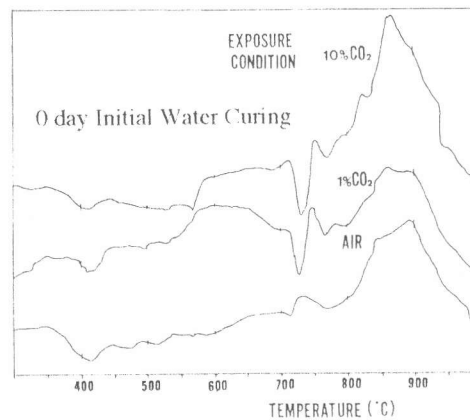


Figure 2. DTA curves of 75%PBFSC mortar exposed to various concentration of CO₂ for 1 year

(2) Devitrification

Ramachandran, V.S.[4] reported that a granulated slag heated to temperature of 800-900°C shows devitrification accompanied by an evolution of heat, and this is registered as one or more exothermic peaks in a thermogram. The temperature, the number and the intensity of the exothermic peaks differ from slag to slag. In case of PBFSC (Portland Blast-Furnace Slag Cement), the area of exothermic peaks in the DTA may be used conveniently to estimate the glassy phase. The ground Portland cement clinker does not exhibit any peak at 800-900°C and hence does not interfere with exothermic devitrification effects. It was reported that the area under the exothermic peaks is proportional to the slag content in PBFSC. In this paper, it has been obtained that for 75%PBFSC mortar with one day cured in moist room, the area under exothermic peak of mortar exposed to 10% CO₂ is larger than those of mortar exposed to 1% CO₂ or air with 0.07% CO₂ (as shown in Figure 2). This may indicate that the unhydrated slag content in mortar exposed to 10% CO₂ is higher than those in mortar exposed to 1% or 0.07% CO₂. The Ca(OH)₂ in mortar exposed to 10% CO₂ is consumed faster than in those exposed to lower concentration of CO₂. The absence of Ca(OH)₂ may cause the stop of slag hydration. Therefore, it is reasonable that the unhydrated slag content of mortar exposed to 10% CO₂ is largest. This may become one of the reasons why compressive strength of 75%PBFSC mortar exposed to 10% CO₂ is lower than those exposed to 1% CO₂ although both of them are

Table 3. Strength and pore structure of 75%PBFSC mortar at 1 year exposure period (without Initial Water Curing)

		Comp. Strength (kgf/cm ²)	Capillary Porosity (cc/cc)	Total Porosity (cc/cc)
Exposure Condition	10% CO ₂	73.59	0.2530	0.2552
	1% CO ₂	101.01	0.2412	0.2435
	Air	157.54	0.2443	0.2502

completely carbonated (see Table 3). By observing the pore structure, there is only slight difference in their porosity. Therefore, the larger amount of unhydrated slag in mortar may cause the lower compressive strength.

3.2 MECHANICAL PROPERTIES OF CARBONATED MORTAR

(1) Modulus of elasticity and its relation with compressive strength

Since compressive strength of mortar is affected by carbonation considerably[1], the modulus of elasticity should also change due to its unique relation with the compressive strength. Some empirical relationships between modulus of elasticity and compressive strength of concrete are available. However, they cannot be used for mortar. From experimental data, which was obtained at 52 weeks (1 year) exposure period, the relationship between modulus of elasticity and compressive strength of mortar may be proposed as follows,

$$E = k \cdot \sigma_c^{0.75} \quad (1)$$

where E and σ_c are modulus of elasticity and compressive strength of mortar respectively.

Table 4. Carbonated volume fraction of cylindrical mortar at 1 year exposure period

		0 day Initial Water Curing			28 days Initial Water Curing		
		OPC	50%PBFSC	75%PBFSC	OPC	50%PBFSC	75%PBFSC
Exposure Condition	0.07% CO ₂	50%	68.52%	83.39%	18.39%	27.30%	40.13%
	1% CO ₂	100%	100%	100%	32.60%	53.30%	100%
	10% CO ₂	100%	100%	100%	60.93%	83.35%	100%
	Cyclic	21.74%	79.53%	94.46%	10.25%	51.45%	95.45%

Although the carbonated volume fraction is various (as shown in Table 4), the value of k seems to be one value except for blended cement mortar which were initially cured in water for 28 days and conditioned to accelerated carbonation. Figure 3 shows that blended cement mortar initially

cured in water for 28 days gives the lower k value if they are exposed to high concentration of CO₂ where it is more pronounced for 75%PBFSC mortar. It means that for blended mortar initially cured in water for 28 days, carbonation causes the comparatively lower stiffness for similar compressive strength. For blended cement mortar exposed to cyclic condition, the k value was supposed to be in between those exposed to high concentration of CO₂ and those cured in water. However, it can be noticed that the k value is closer to those cured in water. Therefore, for high slag content cement mortar, carbonation does not only hinder the strength development (for those without initial water curing) but also reduces the stiffness (for those with 28 days initial water curing).

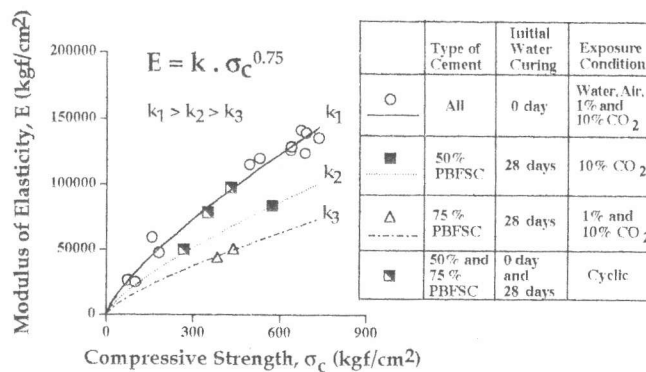


Figure 3. Relationship between Modulus of Elasticity and Compressive Strength

(2) Modulus of elasticity and its relation with capillary porosity

The effect of carbonation on modulus of elasticity of mortar may come through change in porosity. It is generally agreed that, as with strength, the most important factor controlling the modulus of elasticity (E) of hardened cement paste is the porosity. In this paper, the empirical

relationship between modulus of elasticity and capillary porosity of mortar was found to be:

$$E = E_0 \exp(-bP_c) \quad (2)$$

where E_0 is the modulus of elasticity at zero porosity, P_c is the capillary porosity and b is a constant. Figure 4 shows these relationships which seemed to be affected by carbonation. It was found that blended cement mortar initially cured in water for 28 days gives lower E_0 where it is more pronounced for 75% PBFSC mortar. This tendency is quite similar with what was shown in Figure 3. This is a reasonable phenomenon since there is a specific relationship between compressive strength and capillary porosity of mortar.

(3) σ - ϵ curves

In order to understand how carbonation affects the mechanical behavior more clearly, the σ - ϵ curves of mortar with 52 weeks exposure period are presented here. For OPC mortar without initial water curing exposed to high concentration of CO_2 , it is comparatively more "brittle" and has higher compressive strength than those cured in water (see Figure 5). However, for blended cement mortar with 28 days initial water curing exposed to high or normal concentration of CO_2 , it is comparatively lower in the compressive strength and "brittleness" than those cured in water (shown in Figures 6-7).

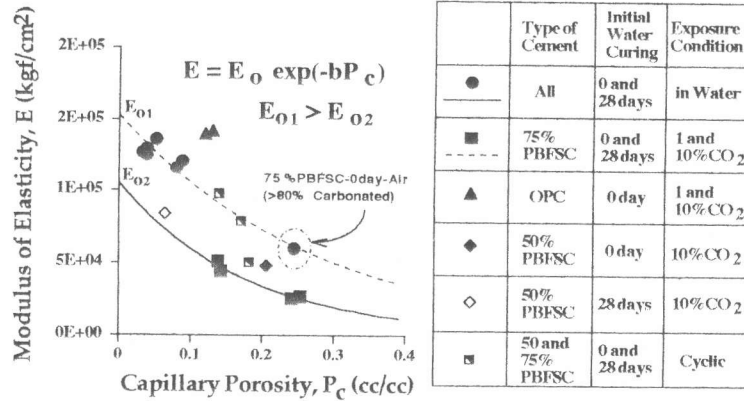


Figure 4. Relationship between Modulus of Elasticity and Capillary Porosity

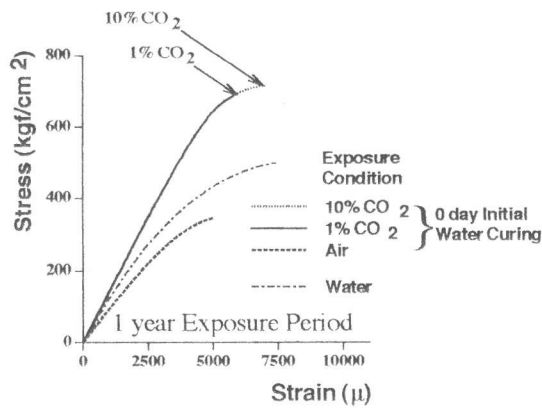


Figure 5. Stress-strain curve of OPC mortar

From σ - ϵ curves, the relationship between ultimate strain and ultimate stress can be found. For concrete, Popovics, S.[5] suggested that this relationship could be assumed as;

$$\epsilon_0 = A \cdot \sqrt[4]{\sigma_0} \quad (3)$$

where ϵ_0 and σ_0 are ultimate strain and ultimate stress respectively and A is a constant. Figure 8 shows the relationship between ϵ_0 and σ_0 , it was found that the deviation is quite large. However, it still can be classified into three groups. The value of A for group I (75%PBFSC carbonated mortar with 28 days initial water curing exposed to CO_2) is the highest which is followed by group II (50%PBFSC carbonated mortar with 28 days initial water curing) and group III (others) respectively. The higher value of A means that the ultimate strain is higher for the same compressive strength. This coincides with what is shown in Figures 3-4.

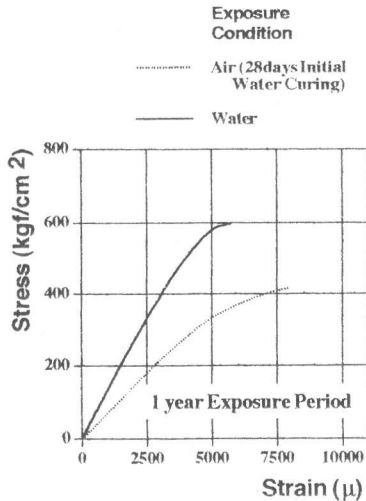


Figure 6. Stress-strain curves of 50%PBFSC mortar

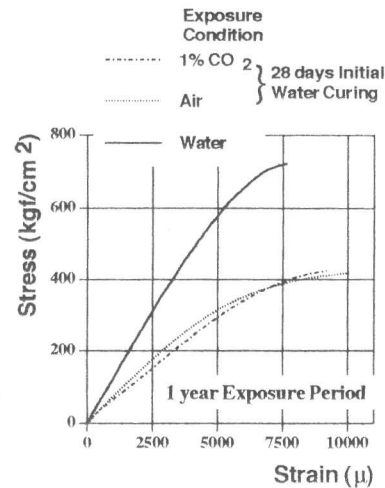


Figure 7. Stress-strain curves of 75%PBFSC mortar

4. CONCLUSIONS

1. Two forms of CaCO_3 , poorly and well crystallized originated by carbonation, was found by differential thermal analysis.
2. For PBFSC mortar, the area of exothermic peaks at $800\text{-}900^\circ\text{C}$ in the DTA may be used conveniently to estimate unhydrated slag.
3. The compressive strength of 75%PBFSC exposed to higher concentration of CO_2 is lower due to the hindrance of slag hydration. This can be noticed by observing the amount of unhydrated slag.
4. Effect of carbonation on elastic modulus and stress-strain curve of mortar depends on type of cement, exposure condition and initial water curing.
5. Carbonation of mortar made by using high slag content does not only hinder its strength development but also reduces its stiffness.

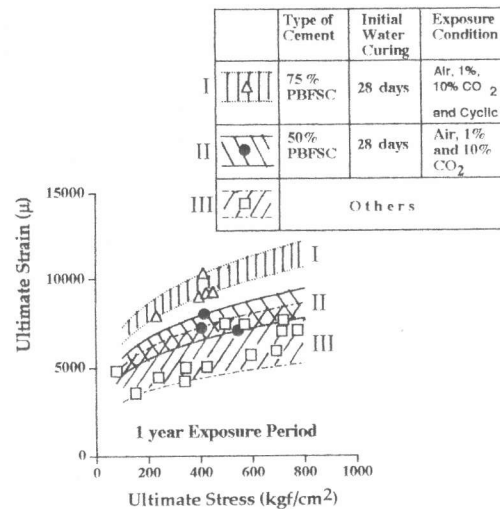


Figure 8. Relationship between Ultimate Strain and Ultimate Stress

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