Scientific paper

Carbonation Reaction of Calcium Silicate Hydrates by Hydrothermal Synthesis at 150°C in OPC- γ -Ca₂SiO₄- α -Quartz Systems

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Abstract

In order to develop organic-fiber reinforced building materials with long-term stability and durability, the carbonation of autoclaved calcium silicate hydrate hardening bodies, prepared by low-temperature synthesis (150°C) in Ordinary Portland Cement (OPC)- γ -Ca₂SiO₄ (γ -C₂S)- α -quartz systems, has been investigated. The CO₂ absorption decreased remarkably as the water-to-powder ratio (w/p) of the samples decreased, and the carbonation of the samples was inhibited. In addition, this tendency became remarkable by the use of γ -C₂S, and carbonation was fully inhibited in the case where the mass ratio of the starting materials OPC, γ -C₂S and α -quartz was 1:4:5. It is estimated that only vaterite, which was based on residual γ -C₂S after accelerated carbonation and had a lower density than calcite and aragonite, filled the pores and densified the sample.

1. Introduction

Fiber-reinforced building materials have been widely used in the fabrication of outer wall and roof materials for use in the construction of houses, and the long-term durability of these materials is a recent requirement in conjunction with the desire for quality assurance in the construction of houses. Therefore, the dimensional and long-term stability of these materials is very important, and it is considered essential that crystalline 1.1 nm tobermorite (5CaO·6SiO₂·5H₂O) be generated in these materials by autoclaved curing at 180°C where it is easy to generate crystalline 1.1 nm tobermorite.

Until the 1990s, asbestos was widely used in Japan as a reinforcement fiber in these building materials, because of its 180°C heat resistance. However, these days, the use of asbestos in construction materials is totally prohibited (by the Labour and Welfare Ministry in Japan), and now organic fibers such as polypropylene and cellulose are widely used as asbestos substitutes.

However, when various organic fibers are used as reinforcement fibers in these materials, it is necessary to lower the temperature of the autoclaved curing from 180°C to 150°C, because of the low-heat resistance of the organic fibers, and low-crystalline or gel-like calcium silicate hydrates are generated in these materials under the existing methods. Therefore, it is necessary that crystalline calcium silicate hydrates such as 1.1 nm tobermorite be prepared synthetically in Ordinary Portland Cement (OPC)- α -quartz systems below 150°C, conditions under which various organic fibers can be used.

In addition, aging deterioration brought about by carbonation of building materials with autoclaved calcium silicate hydrates, such as Autoclaved Aerated Concrete (AAC), has become a serious matter recently. Aging deterioration causes shrinkage and contraction cracks within these materials (Matsushita *et al.* 2004). Therefore, it is necessary that building materials with autoclaved calcium silicate hydrates and carbonation inhibition characteristics be synthesized.

For the purpose of developing organic-fiber reinforced building materials with long-term stability and durability, this research focuses on the effect of an admixture of γ -Ca₂SiO₄ (γ -C₂S) on the crystallinity by low-temperature synthesis at 150°C of autoclaved calcium silicate hydrates, and the carbonation inhibition of its hardening body in OPC- α -quartz systems admixed with γ -C₂S.

2. Experimental details

2.1 Sample preparation

The chemical compositions of OPC, γ -C₂S and α -quartz are shown in **Table 1** and the mineral composition of OPC, calculated by the Rietveld method, is shown in **Table 2**. γ -C₂S was prepared synthetically from the calcium carbonates and the silica sand of industrial materials with a rotary kiln at 1450 °C.

Gamma C₂S was admixed with 0, 20, 40, 60, 80 and 100% OPC to provide a source of lime. The lime source (OPC+ γ -C₂S) and α -quartz were mixed in a ratio of 5:5 and deionized water was added to the powder at water-to-powder ratios (w/p) of 0.3 and 0.5 (mass ratio). At a w/p ratio of 0.3, a polycarboxylic-acid type super-plasticizer was added at 0.5 mass% based upon the powder mass. The prepared paste was held in a moldering flask (volume of 1×1×8 cm) at 100% relative humidity (RH) for 10 hours, and then removed from the flask and autoclaved for 8 hours at 150°C.

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Table 1 Chemical composition and fineness of OPC, γ -C₂S and α -quartz.

Chemical composition (mass %)							Blaine specific surface area (cm ² /g)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	f.CaO	
OPC	21.6	5.08	2.93	64.5	1.95	0.4	3000
α -Quartz	95.9	1.54	0.99	0	0	0	8000
γ -C ₂ S	35.0	1.70	0.10	61.9			3000

Table 2 Mineral composition of OPC (mass%, Calculated by using the Rietveld method).

C ₃ S(Alite)	C ₂ S(Belite)	C ₄ AF	C ₃ A_cubic	Lime	Periclase	Gypsum
59.08	18.80	8.85	4.43	0.918	0.636	0.715
Hemihydrate	Anhydrite	Portlandite	Calcite	C ₃ A_ortho	α -quartz	
1.40	1.38	0	2.00	1.80	0	

Accelerated carbonation of the samples was carried out in CO₂ concentration 5vol% at 20°C and 60% RH for 0, 1, 3, 7, 14, 21, 28, 35, 42, 49, 56, 63 and 70 days. After carbonation, each sample was dipped into a large volume of acetone at 20°C for 30 minutes under reduced pressure (20°C, 2.33×10^3 Pa), in order to terminate the hydration. Afterwards, reduced pressure drying and D-drying (6.666×10^{-2} Pa) were carried out for 24 hours for each analysis.

2.2 Chemical analysis and microscopy

The samples were grinded to give a sample with 1 mm of material removed from the surface (the surface part), and these ground samples were then crushed. Thermogravimetric analysis (TGA, Mac Science WS002) of the samples was performed at a heating rate of 10°C/min. under nitrogen from 20°C and 1000°C. Portlandite (Ca(OH)₂) and calcium carbonate (CaCO₃) contents were determined by weight loss between 405–415°C and 600–800°C, respectively.

X-ray diffraction (XRD) data were collected using a Mac Science XPRESS and a PANalytical X'Pert Pro MPD diffractometer in a θ - θ configuration employing CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The samples were scanned between 5° and 70° with an X'Celerator detector. The ground powders were manually front loaded into a standard circular sample holder (3.5 cm diameter) by lightly pressing with a frosted glass side. 1.1 nm tobermorite was identified from the (002) peak. The crystallite diameter was estimated using the Scherrer equation (Azaroff 1968).

$$L = \frac{k\lambda}{B \cos \theta} \quad (1)$$

where L is the microcrystallite size, k the Scherrer parameter ($k = 0.9$), λ the wavelength of the X-ray beam (1.54 Å), B the full-width at half maximum, and θ the Bragg angle.

The reaction ratios of C₃S and γ -C₂S were calculated from the residual amount by XRD using the internal reference (α -Al₂O₃) method. The quantity of residual C₃S and γ -C₂S was determined by using the integrating area of the diffraction line (620), (040) for C₃S and (130) for γ -C₂S. The reaction rate of α -quartz was measured by quantitative determination of the residual α -quartz with $2 \text{ mol} \cdot \text{dm}^{-3}$ HCl and 5mass% NaCO₃ (Osawa *et al.* 1999). The CaO/SiO₂ ratio of the hydrates was calculated from the reaction ratios of C₃S, γ -C₂S and α -quartz in the samples, assuming that the CaO and SiO₂ in C₃S, γ -C₂S and α -quartz were entirely included in the hydrates.

Scanning Electron Microscope (JSM-5310: accelerating voltage; 20 KV, resolution performance; 4 nm) imaging was utilized to observe the microstructure of the hardened body and pore size distribution, while the cumulative pore volume was measured using a mercury porosimeter (CE INSTRUMENTS Pascal240, pressure range: 0.1–200 MPa).

3. Results and discussion

3.1 Calcium silicate hydrates by hydrothermal synthesis at 150°C

X Ray Diffraction patterns of the surface part with w/p ratios of 0.5 after 8 hours autoclave curing at 150°C, are shown in Fig. 1 and Fig. 2. XRD patterns of the surface part with w/p ratios of 0.3 are shown in Fig. 3. The "T" in the figure corresponds to crystalline 1.1nm tobermorite, while "C" is C-S-H(2), which is quasi-crystalline calcium silicate hydrates, " γ " is C₂S and "S" is sericite (KAl₂(OH)₂AlSi₃O₁₀), which represents the impurities included in α -quartz. Figure 4 and Table 3 show the crystallite diameter and the intensity ratios of diffraction line (222) and (220) for 1.1 nm tobermorite (Kalousek 1969), for the w/p ratios of 0.5 and 0.3.

1.1 nm tobermorite increased as γ -C₂S was admixed with OPC. The peak intensity was the highest with a γ -C₂S replacement ratio of 80%. The crystallite diameter

T : 1.1 nm tobermorite, S : sericite ($\text{KAl}_2(\text{OH})_2\text{AlSi}_3\text{O}_{10}$)

Fig. 1 XRD patterns of the samples with $\gamma\text{-C}_2\text{S}$ at $W/P=0.5$.

T : 1.1 nm tobermorite, $\gamma\text{-C}_2\text{S}$

Fig. 2 XRD patterns of the samples with $\gamma\text{-C}_2\text{S}$ at $W/P=0.5$.

T : 1.1 nm tobermorite, S : sericite ($\text{KAl}_2(\text{OH})_2\text{AlSi}_3\text{O}_{10}$),
C : C-S-H(2)

Fig. 3 XRD patterns of the samples with $\gamma\text{-C}_2\text{S}$ at $W/P=0.3$.

Fig. 4 Crystal diameter of (002) diffraction of 1.1 nm tobermorite by $\gamma\text{-C}_2\text{S}$ at $W/P=0.5$ and 0.3 .

of 1.1 nm tobermorite along the (002) direction gradually increased as the replacement ratio of $\gamma\text{-C}_2\text{S}$ increased, and attained the highest value at a replacement ratio of 80%. By the same token, the intensity ratios of diffraction line (222) and (220) for 1.1 nm tobermorite was highest at a replacement ratio of 80%. Therefore, the crystallinity of 1.1 nm tobermorite gradually increased

with respect to the replacement ratio of $\gamma\text{-C}_2\text{S}$ (Hara and Midgley 1980).

At a w/p ratio of 0.3, as in the case of w/p=0.5, the peak intensity of 1.1 nm tobermorite increased as $\gamma\text{-C}_2\text{S}$ was admixed with OPC, where the highest value was attained with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80%. On the other hand, the 1.1 nm tobermorite peak with $\gamma\text{-C}_2\text{S}$

Table 3 The intensity ratios of diffraction line (222) and (220) for 1.1 nm tobermorite, with the w/p ratios of 0.5 and 0.3.

Replacement ratio of $\gamma\text{-C}_2\text{S}$ (mass%)	0	20	40	60	80	100
W/P=0.5	0	0	0	0.45	0.55	0
W/P=0.3	0	0	0	0	0.43	0

replacement ratios of 0 and 100% could not be identified by XRD. T. Saito (2007) reported that the crystallinity of the 1.1 nm tobermorite in the samples with 0.3 and 0.2 w/p ratios deteriorated in comparison with the samples having w/p ratios greater than 0.5 at 180°C in autoclaved OPC- α -quartz systems. Therefore, admixing OPC with γ -C₂S improved the generation of crystalline 1.1 nm tobermorite even if the w/p ratios of the samples decreased and the autoclave temperature fell to 150°C. In addition, C-S-H(2) was generated in the case where γ -C₂S and OPC were admixed with a w/p ratio of 0.3, but not with a w/p ratio of 0.5. The peak intensity was the highest with a γ -C₂S replacement ratio of 100%. Moreover, other productions, such as killchoanite and calciochondrodite reported by Asaga *et al.* (1981), were not identified in this condition.

Residual γ -C₂S was found to be greater than the γ -C₂S replacement ratio of 20% and Ca(OH)₂ was not in any of the samples due to the pozzolanic reaction with α -quartz during autoclave curing.

Figure 5a to 5c show SEM micrographs of the hardening bodies at w/p ratios of 0.3 with different γ -C₂S replacement ratios, respectively.

Gel-like hydrates were generated in the majority of the sample with a γ -C₂S replacement ratio of 0%, although fibrous hydrates were generated in a small part of the hardening bodies (**Fig. 5a**), and fibrous aggregates were observed with a γ -C₂S replacement ratio of 40% (**Fig. 5b**).

With a γ -C₂S replacement ratio of 80%, plate-type crystalline 1.1 nm tobermorite was generated on the surface of the particles over wide areas (**Fig. 5c**) (Mitsuda *et al.* 1989; Okada *et al.* 1994).

The reaction degree of C₃S in OPC, γ -C₂S and α -quartz with w/p ratios of 0.5 and 0.3 after 8 hours autoclave curing at 150°C are shown in **Fig. 6a** and **Fig. 6b**. The reaction degree of C₃S increased with the replacement ratio of γ -C₂S at w/p ratios of 0.5 and 0.3. A similar trend was observed for the reaction degree of γ -C₂S, except when a replacement ratio of 100% was investigated. On the other hand, the reaction degree of α -quartz was nearly constant at both 0.5 and 0.3 w/p ratios, again with the exception of the 100% replacement ratio. At the 100% replacement ratio, both γ -C₂S and α -quartz hardly reacted after autoclave curing for 8 hours at 150°C.

Figure 7 shows the CaO/SiO₂ ratio of the hydrates, which were calculated from the reaction rates of C₃S, γ -C₂S and α -quartz. The CaO/SiO₂ ratio of 1.1 nm tobermorite (5CaO•6SiO₂•5H₂O) is 0.83.

The CaO/SiO₂ ratio of the hydrates was much higher than the CaO/SiO₂ ratio of 1.1 nm tobermorite (0.83), particularly in the case when γ -C₂S was not replaced for OPC (with a γ -C₂S replacement ratio of 0%).

At w/p ratios of 0.5 and 0.3, the CaO/SiO₂ ratio of the hydrates gradually decreased as γ -C₂S was admixed with OPC, and the CaO/SiO₂ ratio obtained with 60 and 80% γ -C₂S replacement ratios was almost 0.83, which corre-

Fig.5a-c SEM micrographs of the hardening bodies with W/P=0.3 in OPC- γ -C₂S-Q systems which were replaced 0%, 40% and 80% by γ -C₂S respectively.

(a) : 0% (b) : 40% (c) : 80%

sponds to a CaO/SiO₂ ratio of 1.1 nm tobermorite. T. Saito (2007) has already reported that the crystallinity of the hydrates improves as the CaO/SiO₂ ratio decreases and approaches 0.83 for the CaO/SiO₂ ratio of 1.1 nm tobermorite. As shown in **Fig. 1**, the reason why the large peak of 1.1 nm tobermorite can be identified by XRD with γ -C₂S replacement ratios of 60 and 80%, might be that the CaO/SiO₂ ratio decreases, moving closer to the CaO/SiO₂ ratio (0.83) of 1.1 nm tobermorite.

3.2 Carbonation of hardening samples

Figure 8 shows a plot representing CaCO_3 production (the surface part of the samples) obtained from the weight loss between 600-800°C measured by TGA after

Fig. 6a Reaction ratio of Alite in OPC- $\gamma\text{-C}_2\text{S}$ - α -quartz systems.

Fig. 6b Reaction ratio of $\gamma\text{-C}_2\text{S}$ and α -quartz in OPC- $\gamma\text{-C}_2\text{S}$ - α -quartz systems.

Fig. 7 The CaO/SiO_2 ratio of the calcium silicate hydrates in OPC- $\gamma\text{-C}_2\text{S}$ - α -quartz systems.

accelerated carbonation of the samples with w/p ratios of 0.5 and 0.3.

At a w/p ratio of 0.5, CaCO_3 production increased until the 14th day, where production became almost constant. CaCO_3 production was almost the same value at replacement ratios of 0 and 40%, and it was not until the 70th day that CaCO_3 production rose to a slightly higher value at a replacement ratio of 80%.

By comparison with CaCO_3 production at a w/p ratio of 0.5, production at a w/p ratio of 0.3 showed a gradual increase that continued until the 28th day at a replacement ratio of 80%, and until the 70th day at replacement ratios of 0 and 40%.

As in the case of a w/p ratio of 0.5, CaCO_3 production had almost the same value at replacement ratios of 0 and 40% until the 70th day. However, CaCO_3 production sharply decreased at a replacement ratio of 80%, and was only 5 mass% of the total weight of the sample.

Figure 9 shows the relationship between pore size diameter and cumulative pore volume of hardened bodies before (0 days) and after 28 days of the accelerated carbonation replaced by $\gamma\text{-C}_2\text{S}$ at W/P=0.3.

Before the accelerated carbonation (0 days), there were no differences in any of the samples, while pore size diameter shifted to a larger one on the 28th day after the accelerated carbonation, as the replacement ratio of $\gamma\text{-C}_2\text{S}$ decreased. Particularly, at a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80%, there was no difference in pore size diameter and cumulative pore volume after the 28th day.

Therefore, carbonation was fully inhibited at a w/p ratio of 0.3 and at a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80% (mass ratio of starting materials OPC, $\gamma\text{-C}_2\text{S}$ and α -quartz was 1:4:5).

3.3 X-Ray Diffraction of carbonated samples after accelerated carbonation

Figure 10a to 10c and Figure 11a to 11c show the variations in peak intensities on the surface part of XRD of 1.1 nm tobermorite, C-S-H(2), $\gamma\text{-C}_2\text{S}$ and the respective CaCO_3 peak at w/p ratios of 0.5 and 0.3. These results were determined by using the (002) diffraction for 1.1 nm tobermorite, the (100) diffraction for C-S-H(2), the (130) diffraction for $\gamma\text{-C}_2\text{S}$, the (104) diffraction for calcite, the (110) diffraction for vaterite, and the (111) diffraction for aragonite.

With a $\gamma\text{-C}_2\text{S}$ replacement ratio of 0%, the peak intensity of calcite was generated on the 1st day at w/p ratios of both 0.5 and 0.3. The 1.1 nm tobermorite peak intensity decreased, and then the peaks of the CaCO_3 polymorphs, vaterite and aragonite, were generated at a w/p ratio of 0.5 (Saito 2007). Vaterite was generated on the 1st day as a C-S-H(2) peak, which later decreased in intensity. An aragonite peak was generated on the 21st day after the 1.1 nm tobermorite peak intensity decreased at a w/p ratio of 0.3.

With $\gamma\text{-C}_2\text{S}$ replacement ratios of 40 and 80%, calcite was generated except for w/p=0.3 and 80% of $\gamma\text{-C}_2\text{S}$ replacement ratio. In addition, at $\gamma\text{-C}_2\text{S}$ replacement

Fig. 8 The amount of CaCO_3 in carbonated samples determined from the weight loss in the range from 600°C to 800°C .

Fig.9a-b Relationship between pore size diameter and cumulative pore volume of the samples before and after accelerated carbonation replaced by $\gamma\text{-C}_2\text{S}$ at $W/P=0.3$. (a): 0day, (b): 28days

ratios of 40 and 80%, aragonite was identified after the peak of 1.1 nm tobermorite decreased.

On the other hand, vaterite was generated on the 1st day at $w/p=0.5$, on the 7th day at $w/p=0.3$ with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 40%, and on the 14th day at $w/p=0.3$ with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80% as the $\gamma\text{-C}_2\text{S}$ peak decreased. At $w/p=0.3$, and with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80%, the peak of 1.1 nm tobermorite did not decrease and calcite and aragonite were not generated until the 70th day of accelerated carbonation. Therefore, it is estimated that vaterite was generated by carbonation of $\gamma\text{-C}_2\text{S}$ under this experimental condition. In addition, it is necessary that the generation of calcium carbonates be investigated in conjunction with the calcium ion concentration in solution, and the crystal nucleation and growth rate (Suzuki *et al.* 1989; Nakai 1986).

At $w/p=0.3$, and with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 80%, the $\gamma\text{-C}_2\text{S}$ peak was constant after the 7th day, and crystalline 1.1 nm tobermorite remained in the material on the 70th day. On the other hand, at $w/p=0.3$ and with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 40%, the $\gamma\text{-C}_2\text{S}$ peak contin-

ued to decrease until the 70th day.

Figure 12a to 12c show SEM micrographs of the hardening bodies at w/p ratios of 0.3 with different $\gamma\text{-C}_2\text{S}$ replacement ratios, in which accelerated carbonation was carried out for 28 days.

On the 28th day of accelerated carbonation, no fibrous hydrates were observed when the $\gamma\text{-C}_2\text{S}$ replacement ratio of 0% was used, although gel-like hydrates were observed over wide areas (**Fig. 12a**).

In contrast, the structures of the calcium silicate hydrates with $\gamma\text{-C}_2\text{S}$ replacement ratios of 40% maintained the original fibrous structure in the core part of the sample to some degree, although serious degradation of the hydrates by the carbonation was confirmed in several areas (**Fig. 12b**). The CaCO_3 production with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 40% was about the same as that produced with a $\gamma\text{-C}_2\text{S}$ replacement ratio of 0%, but it is estimated that the morphology of the hydrates after accelerated carbonation was different because the peak of 1.1 nm tobermorite did not decrease (see **Fig. 11b**).

Fig. 10 Peak intensities of respective products of the samples replaced by γ -C₂S at W/P=0.5.
(a): 0% (b): 40% (c): 80%

Fig. 11 Peak intensities of respective products of the samples replaced by γ -C₂S at W/P=0.3.
(a): 0% (b): 40% (c): 80%

With a γ -C₂S replacement ratio of 80%, the original plate-type structure was maintained after carbonation, as observed in the case of 40% (Fig. 12c). This occurs because CaCO₃ production after the 70th day of carbonation was only 5 mass% of the total weight of the sample and carbonation was fully inhibited (Fig. 9).

3.4 Carbonation mechanism of autoclaved calcium silicate hydrates by using γ -Ca₂SiO₄

As shown in Fig. 11b and Fig. 11c, in the case where the w/p ratio of the sample was lowered and γ -C₂S was admixed with OPC, the XRD peaks of 1.1 nm tobermorite and C-S-H(2) did not decrease, and carbonation was fully inhibited during accelerated carbonation. Particularly, at w/p=0.3 with a γ -C₂S replacement ratio of 80%, CaCO₃ production after the 70th day of carbonation was only 5 mass% of the total weight of the sample, which was equivalent to a sample autoclaved in OPC- α -quartz systems with w/p ratios of 0.2 at 180°C (Saito 2007). It is estimated that such an effect of carbonation inhibition is related to the generation of vaterite. Vaterite is less dense than other calcium carbonates such as calcite and aragonite (calcite: 2.711g/cm³, aragonite: 2.944 g/cm³, vaterite: 2.645 g/cm³) (mindat. org – the mineral and locality database). Therefore, it is estimated that only vaterite, which was generated after accelerated carbonation and had a lower density than calcite and aragonite, filled the sample pores and densified the sample.

4. Conclusions

For the purpose of developing organic-fiber reinforced building materials with long-term stability and durability, the crystallinity of autoclaved calcium silicate hydrates and the carbonation of its hardening body by low-temperature synthesis at 150°C in OPC- α -quartz systems admixed with γ -C₂S were investigated and the following conclusions were reached.

- (1) At a w/p ratio of 0.5, the peak intensity of 1.1 nm tobermorite decreased as γ -C₂S was admixed for OPC. The peak was the highest with a γ -C₂S replacement ratio of 80%. By the same token, at a w/p ratio of 0.3, the peak intensity of 1.1 nm tobermorite decreased as γ -C₂S was admixed for OPC, and was the highest with a γ -C₂S replacement ratio of 80%.
- (2) At a w/p ratio of 0.3, and with a γ -C₂S replacement ratio of 80%, the peak of 1.1 nm tobermorite did not decrease during accelerated carbonation, which was fully inhibited. In addition, vaterite was mainly generated by carbonation of γ -C₂S under this experimental condition.
- (3) A hardening body containing crystalline 1.1 nm tobermorite and having excellent carbonation inhibition can be synthesized by autoclaved curing at 150°C, when various organic fibers are available.

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Fig.12a-c SEM micrographs of the hardening bodies with W/P=0.3 after 28 days of accelerated carbonation in OPC- γ -C₂S-Q systems which were replaced 0%, 40% and 80% by γ -C₂S respectively.

(a) : 0% (b) : 40% (c) : 80%

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