

Physical and Chemical Properties of Cement Mortar with Gamma-C₂S

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ABSTRACT

Presently, for the cement industry, studies that seek to reduce CO₂, because of the development of the plastic industry and demand for reduction of energy use, have been actively conducted among them, studies attempting to use Gamma-C₂S(γ -C₂S) to fix CO₂ have been actively conducted. The γ -C₂S compound has an important function in reacting to CO₂ and stiffening through carbonatization in the air. The γ -C₂S compound, reacting to CO₂ in the air, generates CaCO₃ within the pore structure of cement materials and densifies the pore structure this leads to an improvement of the durability and to the characteristic of resistance against neutralization. Therefore, in this experiment, in order to synthesize γ -C₂S, limestone sludge and waste foundry sands are used these materials are plasticized for 30 or 60 minutes at 1450°C, and are prevented from being cooled in the temperature range of 30 ~ 1000°C when they are about to be cooled. XRD analysis and XRF analysis are used to determine the effects of this process on γ -C₂S synthesization, the temperature at which a thing is plasticized, and the conditions for cooling that obtain in the plasticized clinker also, in order to confirm the CO₂ capture function, analysis of the major hydration products is conducted through an analysis of carbonatization depth and compressive strength, and through MIP analysis and XRD Rietveld analysis. As a result of these analyses, it is found that when γ -C₂S was synthesized, the clinker that was plasticized at 1450°C for one hour demonstrated the highest yield rate the sample with which the γ -C₂S was mixed generated CaCO₃ when it reacted with CO₂ therefore, carbonatization depth and porosity were reduced, and the compressive strength was increased.

Key words : CO₂ capture, Pore, Vaterite, Gamma-C₂S

1. Introduction

Recently, environmental issue, CO₂ emission trading system has been emerged globally. Cement industry, among various sectors, is the field that has consumed more resources and energy, resulting in CO₂ emissions totaling 70 million tons annually. Concrete that has long been used in civil and building work comprises mostly cement which is mixed with aggregate, water and admixture and consumption has still been on the rise thanks to such advantages as low price and high strength. Consequently, consumption of cement has been increasingly growing causing CO₂ emissions to rise accordingly and such increase also has caused environmental problem. Thus cement industry has made efforts to reduce CO₂ emissions and one of typical measures taken is adding industrial byproducts including fly ash and furnace slag to cement as admixture and another is CO₂ capture and storage using the characteristics of the mate-

rial. The method of replacing and adding industrial byproducts to cement is the most common way, which however has the problem in achieving early compressive strength comparing to cement. On the other hand, the material for CO₂ capturing and storing is gamma-C₂S(γ -C₂S) which is air hardening material which is not responsive to water, but to CO₂.¹⁾ Based on such γ -C₂S compositing technology, the study on composition using CaCO₃ and sand has been underway and application to the field was attempted in Japan. In this study, waste foundry sand that replaces the natural sand was used as SiO₂ source for the purpose of CO₂ capture and limestone (Yonghyun, Dogye) was used as CaCO₃ source so as to develop and test the way of composing γ -C₂S using waste resource. And fly ash that contains high content of CaO was used as CaO source, thereby reducing CO₂ emissions generated by pyrolysis of limestone. To identify the optimal composition condition for γ -C₂S using waste foundry sand, limestone and fly ash, burning condition and cooling condition were reviewed and the effect on γ -C₂S composition yield depending on substitution by fly ash was checked and γ -C₂S composed was mixed with cement paste to check the performance of CO₂ capture so as to monitor the basic properties and the change to the properties through reaction with CO₂.

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2. Experimental Procedure

2.1. Experiment material

The material used in this experiment was Type I Portland cement (DongYang. Co.Ltd) and the components were as Table 1. Limestone which is the raw material to compose γ -C₂S was taken from Dogye (D-CaCO₃) and Yonghyun (Y-CaCO₃), Gangwon Province and in addition, fly ash which is the byproduct from fluidized-bed boiler and waste foundry sand (WFS) were used and chemical composition of the materials according to XRF analysis is as Table 2. As a result of x-ray diffraction analysis (XRD, Rigaku Ultima II diffractometer, Japan), it's found to have comprised of CaO and CaSO₄ (Fig. 1) and using fly ash, Y-CaCO₃, D-CaCO₃ and WFS, γ -C₂S was composed and each material was dried at 105°C for 24 h and crushed for use.²⁾

2.2 Calcination process

Based on molar ratio of two types of limestone which is CaO source and WFS which is SiO₂ source, limestone and WFS were mixed at 5:1 though it's 2:1 for reagent before pouring into the mould and was produced in pellet form by 20 MPa hand-pressing. According to calcination condition, it was left at 900°C for 30 minutes while increasing the temperature at the rate 10°C/min which was then increased again to 1,450°C at the rate of 10°C/min and maintained for 30 minutes. The the sample underwent furnace cooling to 200°C before taking out from the furnace and cooling at room temperature. Dusting by volume expansion occurred with the sample which was taken out from electric furnace (Fig. 2) and after cooling completely, the sample was crushed by ball mill.³⁾

2.3 Preparation of sample and experiment method

XRD analysis was conducted to identify the components of γ -C₂S quantitatively. Measurement was carried out at 4°/min in the range of 2 theta 0 ~ 80°. Then XRD-Rietveld analysis was conducted for quantitative analysis and for CO₂ capture test using γ -C₂S, mortar sample was produced according to KS L 5105, which underwent water curing at 20°C for 24 h and accelerated curing at RH 65% 40°C for 3

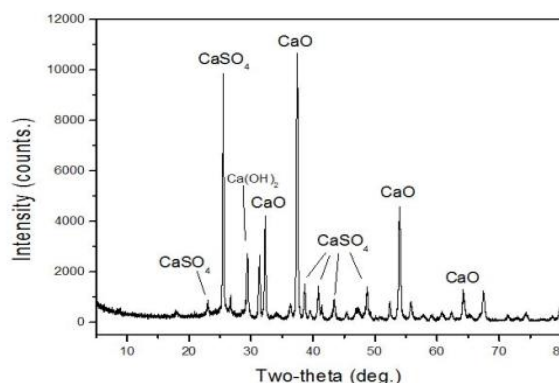


Fig. 1. X-ray diffraction patterns of fly ash.



Fig. 2. Dusting responses during cooling after sintering: (a) Before Sintering, (b) After Sintering

days. The sample after curing process underwent curing process in carbonatization chamber at CO₂ 10%, 20°C, RH 60% for 28 days. Carbonatization depth of the sample was measured by Phenolphthalein method (KS F 2596) Compressive strength test of the samples after carbonatization process was conducted using Universal Testing Machine (UTM) so as to check the effect of γ -C₂S on carbonatization. And to identify the effect of cement hydrate mixed with γ -C₂S in carbonatization process, cement paste by substituting γ -C₂S at 5% and 10%, respectively was produced. Cement paste sample was submerged into acetone for 24 h and dried at 50°C and crushed by ball mill. The grain size after such process was 106 μ m or less and the sample in the form of fine particle was measured by XRD analysis while the porosity of the sample in the form of 2mm bulk was measured (MIP, Micromeritics, Auto pore IV 9520).⁴⁾

Table 1. Physical Properties and Chemical Composition of OPC

SiO ₂ %	Al ₂ O ₃ %	CaO%	MgO%	Fe ₂ O ₃ %	Na ₂ O%	K ₂ O%	SO ₃ %	Specific gravity	Blaine (cm ² /g)
17.30	4.08	66.50	3.02	3.13	0.09	1.33	3.25	3.15	3,412

Table 2. Chemical Composition as Determined by XRF (wt.%)

	CaO	CO ₂	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	Fe ₂ O ₃	SO ₃	Others	Total
Y-CaCO ₃ ^{a)}	51.80	41.10	3.28	2.09	0.50	0.48	0.40	0.0285	0.32	100
D-CaCO ₃ ^{b)}	51.80	43.60	0.68	0.34	2.98	0.09	0.37	0.0366	0.10	100
WFS ^{c)}	0.13	-	97.00	1.83	0.05	0.34	-	-	0.65	100
Fly ash	65.61	-	1.15	0.56	2.57	-	0.62	21.48	7.85	-

^{a)}CaCO₃ - Yonghyun in Korea

^{b)}CaCO₃ - Dogea in Korea

^{c)}Waste foundry sand

3. Results and Discussion

3.1 γ -C₂S composition yield depending on type of CaCO₃

C₂S γ polymorph is generated during the process when β (bet) is converted to γ (gamma) In tetrahedral rotation of SiO₄ and atomic calcium migration, particles are split into smaller particles while the volume is increased by 12% which is called dusting.⁹⁾ Fig. 3 shows diffraction pattern according to XRD analysis of the sample calcinated by mixing D-CaCO₃, Y-CaCO₃, WFS powder. As a result of XRD analysis, with regard to γ -C₂S peak appeared around 2theta 29.5°, peak intensity of the sample using Y-CaCO₃ was higher than the sample using D-CaCO₃. As a result of XRD-Rietveld analysis, the sample using Y-CaCO₃ contained 94.4 wt.% while the sample using D-CaCO₃ contained 46.7 wt.% of γ -C₂S, which indicated that the difference in composition by origin had a significant effect on generation of γ -C₂S, which was attributable to difference in composition yield due to Mg ion used as stabilizer or impurities during composing γ -C₂S when changing from β to γ . Thus, Y-CaCO₃ which generates more γ -C₂S in sample after calcination process was applied to CO₂ capture test.

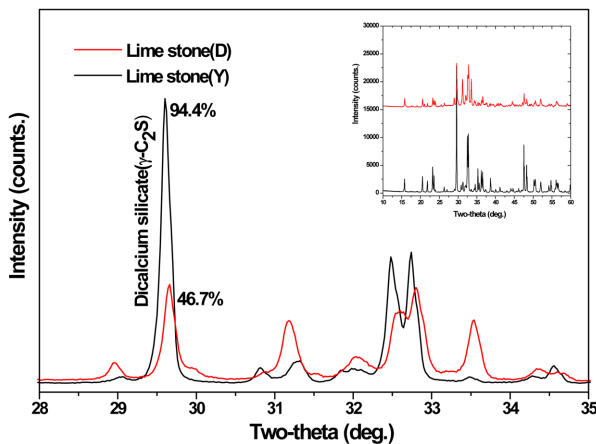


Fig. 3. XRD analysis results of synthesized γ -C₂S.

3.2 Variation of γ -C₂S composition depending on cooling condition

In composition of γ -C₂S using waste resources, the effect of cooling condition after calcination process on γ -C₂S dusting and generation was reviewed. After firing the clinker at 1,450°C for 30 minutes and setting the discharge temperature of electric furnace at 1000, 800, 600, 400, 200 and 30°C, the samples were cooled down at room temperature. Then γ -C₂S peak was checked using XRD analysis. Fig. 4 shows the difference in XRD peak intensity depending on discharge temperature for cooling in composition of γ -C₂S. There's a slight difference in peak of samples after burning at set temperature and discharged at different conditions but the effect of discharge temperature on generation of γ -C₂S was considered insignificant. That is, difference in discharge temperature after burning at set temperature was not influential on phase inversion from β -C₂S to γ -C₂S

3.3 Effect of ash fly on composition of γ -C₂S

Table 3 shows generation of γ -C₂S when replacement rate of fly ash to the limestone to be abandoned after cement manufacture is 0, 0.5, 1.0, 3.0 and 5.0 wt.%, which resulted from XRD-Rietveld analysis of the sample produced using Y-CaCO₃ and waste foundry sand (WFS) Replacement rate

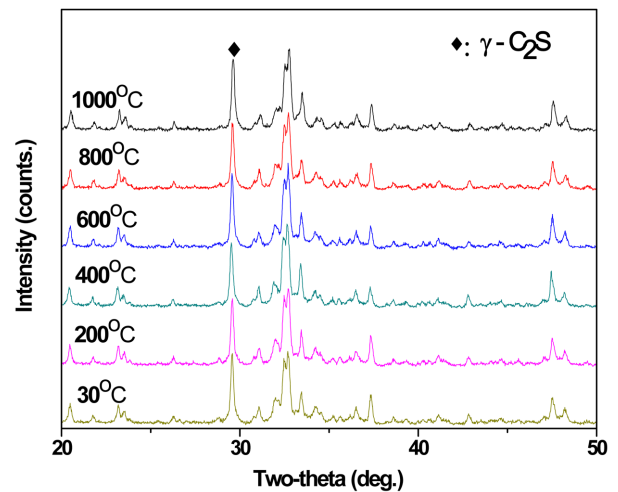


Fig. 4 XRD analysis results of cooling temperatures.

Table 3. γ -C₂S Yield Variation in Fly Ash Replacement Ratio over the XRD- Rietveld Analysis

Profile ID	Fly ash replacement ratio by weight of CaCO ₃					
	0 wt.%	0.5 wt.%	1.0 wt.%	3.0 wt.%	5.0 wt.%	
Dicalcium silicate - Ca ₂ (SiO ₄)	91.4	78.3	74.6	60.6	37.5	
Calcium silicate - Ca ₂ SiO ₄	-	0.3	1.2	1.6	1.3	
Calcium silicate - Ca(SiO ₃)	-	-	-	-	-	
Lime - CaO	-	11.4	9.3	11.9	16.0	
Larnite - Ca ₂ SiO ₄	-	-	7.7	19.0	38.6	
Akermanite - Ca ₂ Mg(Si ₂ O ₇)	8.6	-	-	-	-	
Hatruite - Ca ₃ SiO ₅	-	10.0	7.2	6.9	6.6	
Total	100.0	100.0	100.0	100.0	100.0	

of fly ash was appeared to have had a significant effect on generation of γ -C₂S. When replacement rate of fly ash is increased, generation of γ -C₂S tends to reduce (Fig. 5) which is attributable to impurities or ion used as stabilizer as shown in the result depending on origin of limestone.⁶⁾ It's reported by previous studies that inversion from β -C₂S to γ -C₂S is constrained by adding proper impurities such as boron. Further study on such impurities is necessary to identify the cause of such phenomenon.

3.4 CO₂ capture of composed γ -C₂S

Composed γ -C₂S was mixed with 7.5 wt.% water and the sample with the density 1,550 kg/m³ was produced through the process of isostatic pressing into a small cylindrical shape and the sample underwent accelerated carbonatization process by exposing to high purity CO₂ for 28 and 56 days, respectively. Fig. 6 shows the result of XRD analysis intended to check CO₂ capture effect of γ -C₂S in each sample. C₂S and Ca(OH)₂ hydrate were detected from the sample which was not exposed to low CO₂ but Ca(OH) peak during CO₂ curing was dissipated after reaction with CO₂ and vaterite CaCO₃ hydrate including calcite CaCO₃ was found which was attributable to vaterite CaCO₃ as a result of reaction of Ca(OH)₂ with CO₂ and the reaction between γ -C₂S and unreacted CaO and CO₂. Thus it's expected that γ -C₂S will collect CO₂ thereby reducing CO₂ in the air and when applying mortar, CaCO₃ product will reduce the porosity and increase the compressive strength.

3.5. Characteristics of compressive strength

Figure 7 shows the compressive strength of cement mortar sample containing γ -C₂S at replacement rate 5 and 10 wt.% and ordinary cement mortar without γ -C₂S. Comparison between mortar sample without carbonatization process and the sample after carbonatization process with 10% CO₂ for 28 days and 56 days was made. When replacing γ -C₂S by 10% or more, hardened cement paste becomes collapsed because of excessive reactivity due to unreactive CaO in γ -C₂S. Viewing the result, the more the replacement rate the less the cement weight and the less the compressive strength before carbonatization process, but in case of the

sample containing carbonized γ -C₂S (γ -C₂S replacement rate 5, 10 wt.%), compressive strength was increased than OPC (γ -C₂S replacement rate 0 wt.%) which was attributable to forming CaCO₃ crystal phase by γ -C₂S through reaction with CO₂ in hardened cement paste that increased the compressive strength by reducing the porus in cement.

3.6 Porosity of hardened cement paste mixed with synthetic γ -C₂S

Figure 8 shows the porosity of mortar sample produced using γ -C₂S which has superior performance in compressive strength and penetration depth in a way of replacing γ -C₂S 10 wt.% before and after carbonatization. A rapid decrease in porosity appeared in porus less than 100 μ m because of CaCO₃ generated by reaction between γ -C₂S and CO₂ at carbonatization condition, comparing to standard condition. Such result is attributable to CaCO₃ generated in porus in hardened cement paste. Porosity was 29.0% at standard curing condition which was reduced to 19.4% when curing

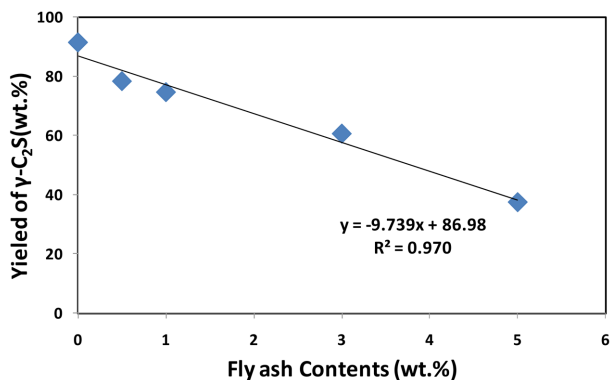


Fig. 5. Yield of γ -C₂S by fly ash replacement ratio.

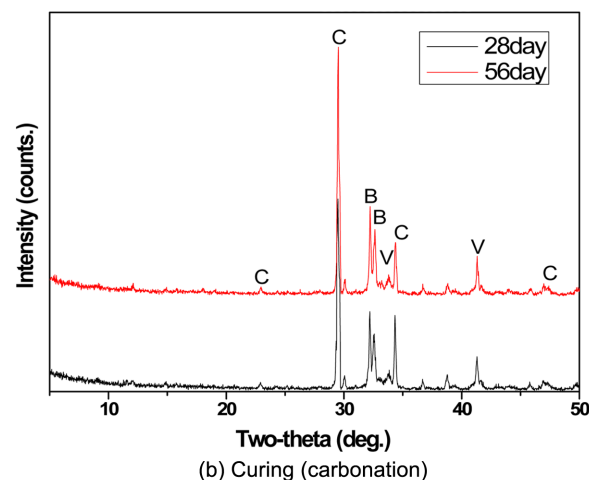
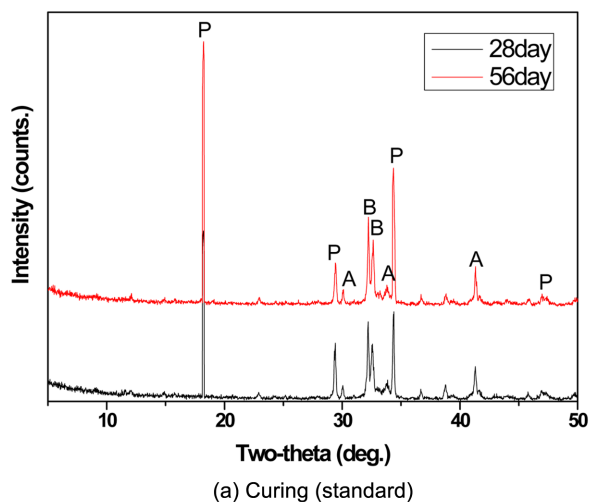


Fig. 6. XRD results of each paste after CO₂ reaction. (a) P : Portlandite(Ca(OH)₂), A : Alite(C₃S), B : Belite(C₂S), (b) C : Calcite(CaCO₃), V :Vaterite(CaCO₃), B : Belite (C₂S)

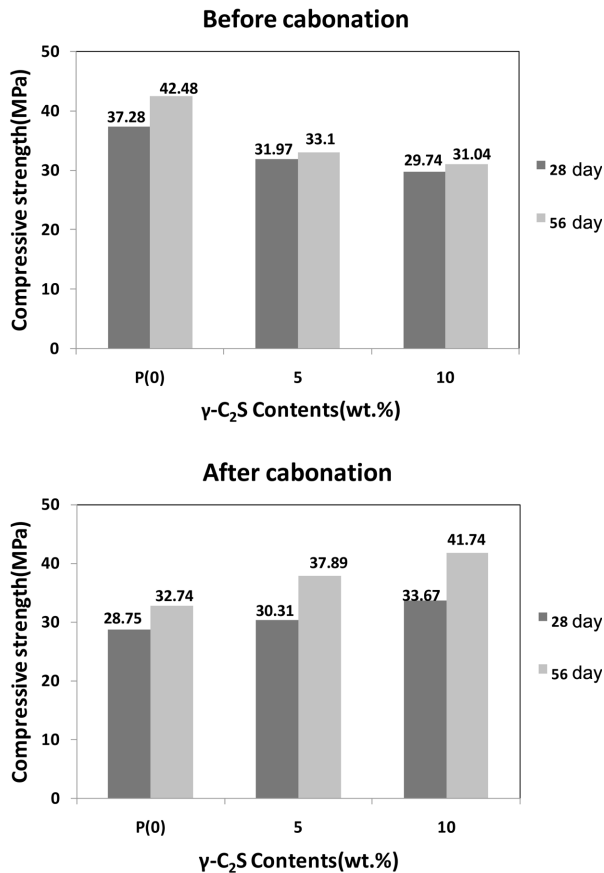


Fig. 7. Changes of compressive strength of mortar.

the same sample at carbonatization condition (Table 4) Such reduction resulted from calcite(CaCO₃) and vaterite(CaCO₃) generated as a result of reaction between γ -C₂S and CO₂ by carbonatization that resulted in densifying the structure.

3.7 Mixing γ -C₂S with hardened cement paste and CO₂ capture

To identify CaCO₃ generated after curing cement mortar by replacing γ -C₂S 10% in carbonatization chamber set as CO₂ density 10%, temperature 20°C and humidity 60% for 56 days, XRD-riedveld analysis was conducted. Viewing the analysis result in Table 5, OPC in case of 19.58%, γ -C₂S replacing, 31.24% of CaCO₃ was generated. Consequently,

Table 4. Porosity Change of Paste Containing γ -C₂S

type	Standard curing	Carbonation curing	Porosity reduction(%)
Porosity(%)	29.0	19.4	33.1

Table 5. CO₂ Capture Rate through Carbonation

type	CaCO ₃ amount		CO ₂ capture (%)
	OPC	γ -C ₂ S (10%)	
Carbonation	19.58%	31.24%	59.5%

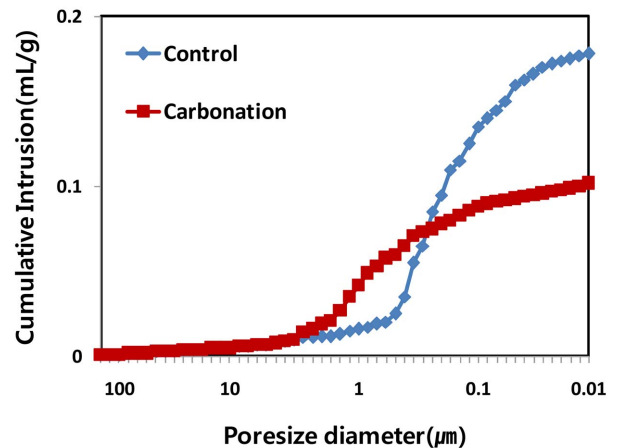


Fig. 8. Porosity analysis of the paste.

CaCO₃ generation by CO₂ capture was more than OPC by 11% and in case of replacing γ -C₂S 10%, 59.5% CO₂ capture was achieved. .

CO₂ emission per ton of cement in Korea is 0.856 ton and when composing γ -C₂S, it's 0.274ton. Thus, in case of replacing γ -C₂S 10%, CO₂ emission would be 0.798 ton which is less than cement and 0.475 ton would be captured by CO₂ capture.

4. Conclusions

1. As a result of accelerated carbonatization of γ -C₂S for 28 & 56 days, vaterite and calcite were formed.
2. According to measuring carbonatization penetration depth, the more replacement of γ -C₂S the less porous and penetration depth because of generation of vaterite and calcite.
3. After carbonatization of mortar by replacing 10 wt.% to OPC, compressive strength of mortar mixed with γ -C₂S with replacement rate 10 wt.% was higher than OPC because of CaCO₃ generated as a result of reaction between γ -C₂S and CO₂ that resulted in densifying the porous.
4. As a result of measuring the porosity of hardened cement paste, porosity of cement paste after replacing γ -C₂S 10 wt.% was less than cement paste without using γ -C₂S by 33.1% which indicated mixing γ -C₂S with hardened cement paste would increase CO₂ capture as well as compressive strength and CO₂ capture rate was 59.5% which is able to achieve the capture of 0.475 ton CO₂ in case of replacing γ -C₂S 10%.

Thus, when replacing and adding γ -C₂S to cement material, CaCO₃ in various phases is generated by reaction between γ -C₂S and CO₂ in the air at early stage which densifies the porous in cement. It creates the effect to enhance the compressive strength more than cement material without γ -C₂S. In cement material exposed to the air containing CO₂, CO₂ is the major cause to neutralize the cement material. But cement material containing γ -C₂S densifies the

poris in cement at early stage so as to retard penetration or expansion of CO₂. That is, cement material containing γ -C₂S performs carbonatization response by CO₂ penetrated from outside which results in densifying the porous structure of cement material at early stage and CO₂ penetration and expansion are delayed. Obviously, it's necessary to identify the relationship between neutralization resistance and CO₂ penetration and expansion so as to verify the effect of optimal use of γ -C₂S.

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