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Physical and Chemical Properties of Cement Mortar with Gamma-C_2S

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ABSTRACT

Presently, for the cement industry, studies that seek to reduce CO_2, 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-C_2S(γ-C_2S) to fix CO_2 have been actively conducted. The γ-C_2S compound has an important function in reacting to CO_2 and stiffening through carbonatization in the air. The γ-C_2S compound, reacting to CO_2 in the air, generates $CaCO_2$ 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-C_2S, 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-C_2S 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 CO_2 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-C_2S was synthesized, the clinker that was plasticized at 1450°C for one hour demonstrated the highest yield rate the sample with which the γ-C_2S was mixed generated $CaCO_3$ when it reacted with CO_2 therefore, carbonatization depth and porosity were reduced, and the compressive strength was increased.

Key words : CO_2 capture, Pore, Vaterite, Gamma-C_2S

1. Introduction

Recently, environmental issue, CO_2 emission trading system has been emerged globally. Cement industry, among various sectors, is the filed that has consumed more resources and energy, resulting in CO_2 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 CO_2 emissions to rise accordingly and such increase also has caused environmental problem. Thus cement industry has made efforts to reduce CO_2 emissions and one of typical measures taken is adding industrial byproducts including fly ash and furnace slag to cement as admixture and another is CO_2 capture and storage using the characteristics of the material. 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 CO_2 capturing and storing is gamma-C_2S(γ-C_2S) which is air hardening material which is not responsive to water, but to CO_2.[1] Based on such γ-C_2S compositing technology, the study on composition using $CaCO_3$ 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 SiO_2 source for the purpose of CO_2 capture and limestone (Yonghyun, Dogye) was used as $CaCO_3$ source so as to develop and test the way of composing γ-C_2S using waste resource. And fly ash that contains high content of CaO was used as CaO source, thereby reducing CO_2 emissions generated by pyrolysis of limestone. To identify the optimal composition condition for γ-C_2S using waste foundry sand, limestone and fly ash, burning condition and cooling condition were reviewed and the effect on γ-C_2S composition yield depending on substitution by fly ash was checked and γ-C_2S composed was mixed with cement paste to check the performance of CO_2 capture so as to monitor the basic properties and the change to the properties through reaction with CO_2.

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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-C_2S was taken from Dogye (D-$CaCO_3$) and Yonghyun (Y-$CaCO_3$), Gangwon Province and in addition, fly ash which is the byproduct from fluidized-bed boiler and waste foundary 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 $CaSO_4$ (Fig. 1) and using fly ash, Y-$CaCO_3$, D-$CaCO_3$ and WFS, γ-C_2S 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 SiO_2 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-C_2S 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 CO_2 capture test using γ-C_2S, 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 days. The sample after curing process underwent curing process in carbonatization chamber at CO_2 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-C_2S on carbonatization. And to identify the effect of cement hydrate mixed with γ-C_2S in carbonatization process, cement paste by substituting γ-C_2S 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 μm 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)]

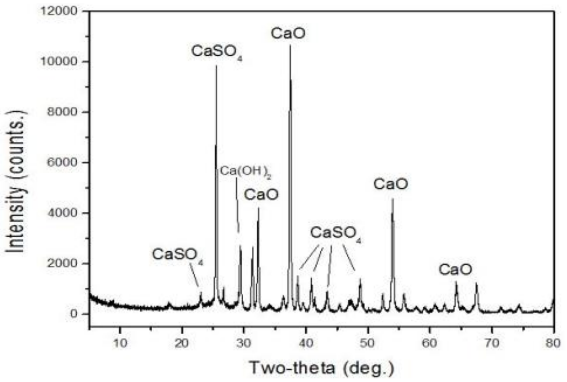

Fig. 1. X-ray diffraction patterns of fly ash.

(a) (b)

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

Table 1. Physical Properties and Chemical Composition of OPC

SiO_2%	Al_2O_3%	CaO%	MgO%	Fe_2O_3%	Na_2O%	K_2O%	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_2O_3	MgO	K_2O	Fe_2O_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)]$CaCO_3$ - Yonghyun in Korea
[b)]$CaCO_3$ - Dogea in Korea
[c)]Waste foundry sand

3. Results and Discussion

3.1 γ -C_2S composition yield depending on type of $CaCO_3$

C_2S γ polymorph is generated during the process when ß (bet) is converted to γ (gamma) In tetrahedral rotation of SiO_4 and atomic calcium migration, particles are split into smaller particles while the volume is increased by 12% which is called dusting.[5] Fig. 3 shows diffraction pattern according to XRD analysis of the sample calcinated by mixing D-$CaCO_3$, Y-$CaCO_3$, WFS powder. As a result of XRD analysis, with regard to γ-C_2S peak appeared around 2theta 29.5°, peak intensity of the sample using Y-$CaCO_3$ was higher than the sample using D-$CaCO_3$. As a result of XRD-Rietveld analysis, the sample using Y-$CaCO_3$ contained 94.4 wt.% while the sample using D-$CaCO_3$ contained 46.7 wt.% of γ-C_2S, which indicated that the difference in composition by origin had a significant effect on generation of γ-C_2S, which was attributable to difference in composition yield due to Mg ion used as stabilizer or impurities during composing γ-C_2S when changing from ß to γ. Thus, Y-$CaCO_3$ which generates more γ-C_2S in sample after calcination process was applied to CO_2 capture test.

3.2 Variation of γ -C_2S composition depending on cooling condition

In composition of γ-C_2S using waste resources, the effect of cooling condition after calcination process on γ-C_2S 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-C_2S 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-C_2S. 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-C_2S was considered insignificant. That is, difference in discharge temperature after burning at set temperature was not influential on phase inversion from ß-C_2S to γ-C_2S

3.3 Effect of ash fly on composition of γ-C_2S

Table 3 shows generation of γ-C_2S 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-$CaCO_3$ and waste foundary sand (WFS) Replacement rate

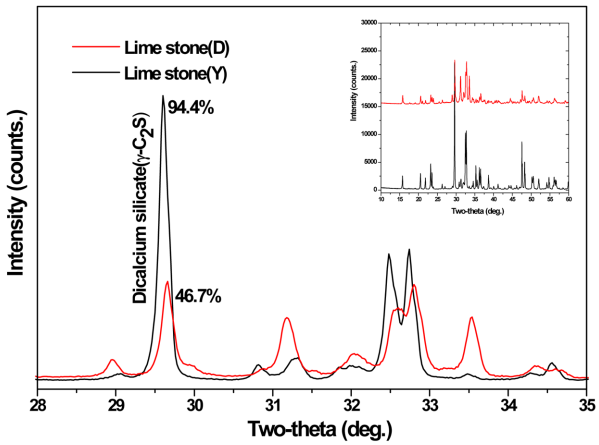

Fig. 3. XRD analysis results of synthesized γ-C2S.

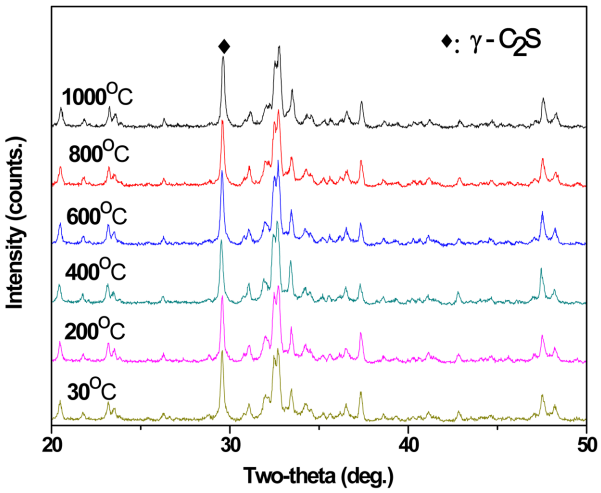

Fig. 4 XRD analysis results of cooling temperatures.

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_2SiO_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_2SiO_4	-	-	7.7	19.0	38.6
Akermanite - $Ca_2Mg(Si_2O_7)$	8.6	-	-	-	-
Hatrurite - Ca_3SiO_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-C_2S. When replacement rate of fly ash is increased, generation of γ-C_2S 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 ß-C_2S to γ-C_2S 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 CO_2 capture of composed γ-C_2S

Composed γ-C_2S was mixed with 7.5 wt.% water and the sample with the density 1,550 kg/m^3 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 CO_2 for 28 and 56 days, respectively. Fig. 6 shows the result of XRD analysis intended to check CO_2 capture effect of γ-C_2S in each sample. C_2S and $Ca(OH)_2$ hydrate were detected from the sample which was not exposed to low CO_2 but Ca(OH) peak during CO_2 curing was dissipated after reaction with CO_2 and vaterite $CaCO_3$ hydrate including calcite $CaCO_3$ was found which was attributable to vaterite $CaCO_3$ as a result of reaction of $Ca(OH)_2$ with CO_2 and the reaction between γ-C_2S and unreacted CaO and CO_2. Thus it's expected that γ-C_2S will collect CO_2 thereby reducing CO_2 in the air and when applying mortar, $CaCO_3$ 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-C_2S at replacement rate 5 and 10 wt..% and ordinary cement mortar without γ-C_2S. Comparison between mortar sample without carbonatization process and the sample after carbonatization process with 10% CO_2 for 28 days and 56 days was made. When replacing γ-C_2S by 10% or more, hardened cement paste becomes collapsed because of excessive reactivity due to unreactive CaO in γ-C_2S. 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-C_2S (γ-C_2S replacement rate 5, 10 wt.%), compressive strength was increased than OPC (γ-C_2S replacement rate 0 wt.%) which was attributable to forming $CaCO_3$ crystal phase by γ-C_2S through reaction with CO_2 in hardened cement paste that increased the compressive strength by reducing the porus in cement.

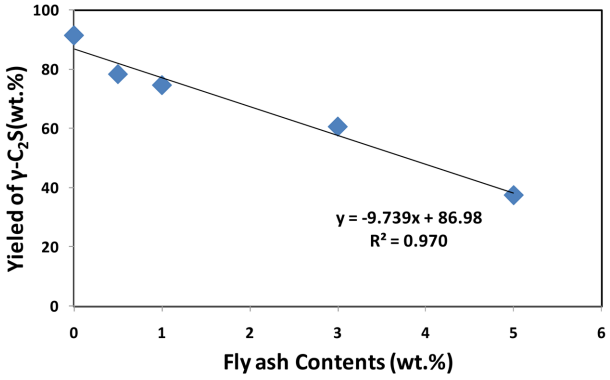

Fig. 5. Yield of γ-C_2S by fly ash replacement ratio.

3.6 Porosity of hardened cement paste mixed with synthetic γ-C_2S

Figure 8 shows the porosity of mortar sample produced using γ-C_2S which has superior performance in compressive strength and penetration depth in a way of replacing γ-C_2S 10 wt.% before and after carbonatization. A rapid decrease in porosity appeared in porus less than 100 μm because of $CaCO_3$ generated by reaction between γ-C_2S and CO_2 at carbonatization condition, comparing to standard condition. Such result is attributable to $CaCO_3$ generated in porus in hardened cement paste. Porosity was 29.0% at standard curing condition which was reduced to 19.4% when curing

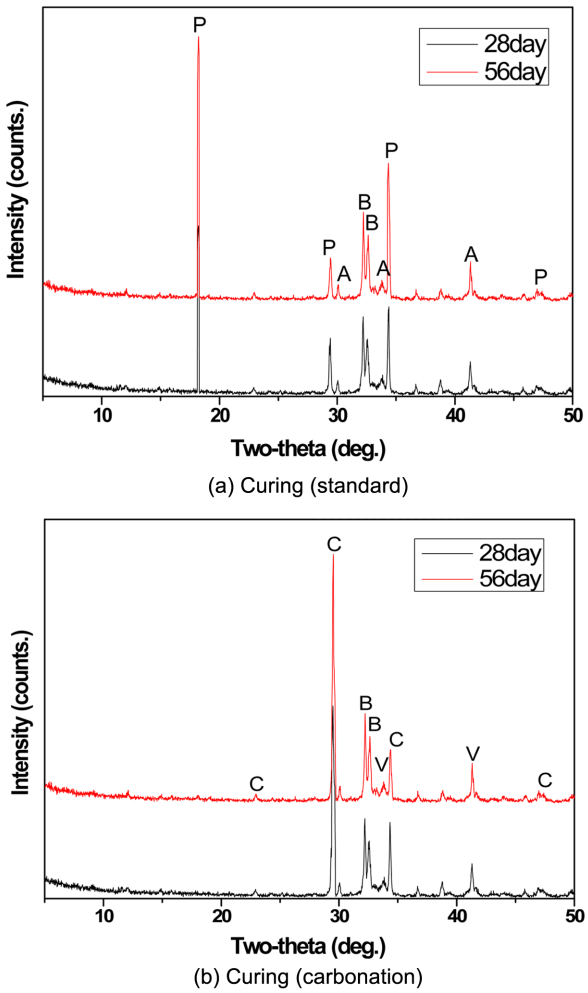

Fig. 6. XRD results of each paste after CO_2 reaction. (a) P : Portrandite($Ca(OH)_2$), A : Alite(C_3S), B : Belite(C_2S), (b) C : Calcite($CaCO_3$), V :Vaterite($CaCO_3$), B : Belite (C_2S)

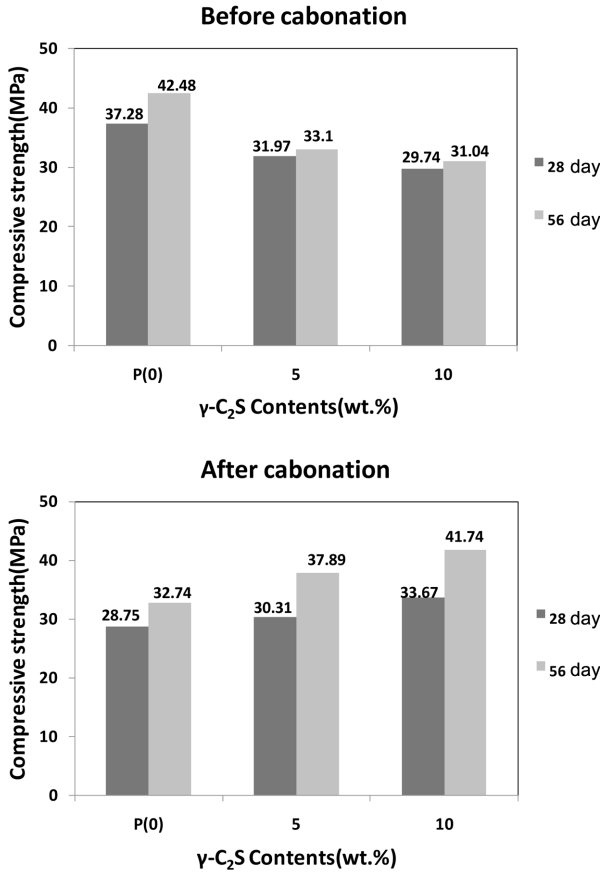

Fig. 7. Changes of compressive strength of mortar.

the same sample at carbonatization condition (Table 4) Such reduction resulted from calcite($CaCO_3$) and vaterite($CaCO_3$) generated as a result of reaction between γ-C_2S and CO_2 by carbonatization that resulted in densifying the structure.

3.7 Mixing γ-C_2S with hardened cement paste and CO_2 capture

To identify $CaCO_3$ generated after curing cement mortar by replacing γ-C_2S 10% in carbonatization chamber set as CO_2 density 10%, temperature 20°C and humidity 60% for 56 days, XRD-rieveld analysis was conducted. Viewing the analysis result in Table 5, OPC in case of 19.58%, γ-C2S replacing, 31.24% of $CaCO_3$ was generated. Consequently,

Table 4. Porosity Change of Paste Containing γ-C_2S

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

Table 5. CO_2 Capture Rate through Carbonation

type	$CaCO_3$ amount		CO_2 capture (%)
	OPC	γ-C_2S (10%)	59.5%
Carbonation	19.58%	31.24%	

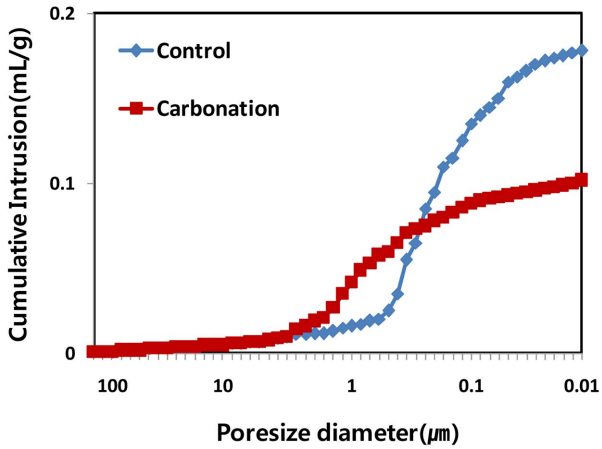

Fig. 8. Porosity analysis of the paste.

$CaCO_3$ generation by CO_2 capture was more than OPC by 11% and in case of replacing γ-C_2S 10%, 59.5% CO_2 capture was achieved. .

CO_2 emission per ton of cement in Korea is 0.856 ton and when composing γ-C_2S, it's 0.274ton. Thus, in case of replacing γ-C_2S 10%, CO_2 emission would be 0.798 ton which is less than cement and 0.475 ton would be captured by CO_2 capture.

4. Conclusions

1. As a result of accelerated carbonatization of γ-C_2S for 28 & 56 days, vaterite and calcite were formed.

2. According to measuring carbonatization penetration depth, the more replacement of γ-C_2S the less porus 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-C_2S with replacement rate 10 wt.% was higher than OPC because of $CaCO_3$ generated as a result of reaction between γ-C_2S and CO_2 that resulted in densifying the porus.

4. As a result of measuring the porosity of hardened cement paste, porosity of cement paste after replacing γ-C_2S 10 wt.% was less than cement paste without using γ-C_2S by 33.1% which indicated mixing γ-C_2S with hardened cement paste would increase CO_2 capture as well as compressive strength and CO_2 capture rate was 59.5% which is able to achieve the capture of 0.475 ton CO_2 in case of replacing γ-C_2S 10%.

Thus, when replacing and adding γ-C_2S to cement material, $CaCO_3$ in various phases is generated by reaction between γ-C_2S and CO_2 in the air at early stage which densifies the porus in cement. It creates the effect to enhance the compressive strength more than cement material without γ-C_2S. In cement material exposed to the air containing CO_2, CO_2 is the major cause to neutralize the cement material. But cement material containing γ-C_2S densifies the

poris in cement at early stage so as to retard penetration or expansion of CO_2. That is, cement material containing γ-C_2S performs carbonatization response by CO_2 penetrated from outside which results in densifying the porus structure of cement material at early stage and CO_2 penetration and expansion are delayed. Obviously, it's necessary to identify the relationship between neutralization resistance and CO_2 penetration and expansion so as to verify the effect of optimal use of γ-C_2S.

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