JOURNALOF

Ceramic Processing Research

CO₂ curing effects of concrete products made using fly ash and blast furnace slag

Jin-O Park^a, Jong-Chan Lee^{b,*} and Sae-Hyun Lee^a

^aBuilding and Urban Research institute, Korea Institute of Civil Engineering and Building Technology, Goyang, Korea ^bBM Tech, Goyang, Korea

In order to analyze the effects of fly ash and blast furnace slag on CO_2 uptake and compressive strengths in CO_2 curing, two tests were carried out. First, the compressive strength test of a non CO_2 cured specimen and a specimen with W/C 30% and 20% admixture was conducted at three hours and three days while curing in a chamber with 20 °C and RH 60% after CO_2 curing for an hour. Second, the compressive strength test of a non CO_2 cured specimen and a specimen with W/C 35-40% and 10% admixture was conducted at 7 days and 28 days while curing in chamber with 60 °C and RH 100% after steam curing at 20 °C and RH 60% and CO_2 curing for 2 hrs. In the first test results, the CO_2 uptake rate of the case with 20% of admixture was found to be 2% lower than the case without admixture, and CO_2 curing turned out to be very effective in increasing the early compressive strength. The second test results showed that CO_2 uptake rate of the case with fly ash and blast furnace slag was found to be similar with the case without admixture. Even in terms of increasing the compressive strength, CO_2 curing of two hours was found to exhibit a similar strength development effect to steam curing of 4 hrs.

Key words: CO₂ curing, Carbonation, Fly ash, Blast furnace slag, Concrete product.

Introduction

As of 2012, global CO₂ emissions reached 34.5 billion tons, of which CO₂ emissions arising from cement production accounted for 9% (3.1 billion tons). The amount of CO2 emissions from Korea was 620 million tons, ranked 7th in the world, of which CO2 emissions released from manufacturing cement were approximately 48 million tons. Therefore, efforts to reduce CO₂ emissions in the cement industry are underway in various ways both in Korea and other countries. In particular, as the Carbon Emissions Trading Scheme started to be implemented in Korea and Germany among the top 10 global emitters of carbon emissions from January 2015, the government enabled companies to buy and sell excess greenhouse emission allowances, and fined companies for the offence of not adhering to emission targets. This has imposed a huge burden on CO₂ emitting companies.

Cement has a characteristic that causes CO_2 emissions but can also store CO_2 by carbonation reaction. This characteristic is referred to as carbonation, and CO_2 is bonded to $Ca(OH)_2$ and C-S-H produced after the hydration reaction of cement to generate $CaCO_3$ in a typical cement carbonation process. However, the carbonation reaction in the initial stage leads to the formation of $CaCO_3$ and C-S-H by follow reactions instead of $Ca(OH)_2$, a product of hydration reaction. $C_{3}S + (3 x)CO_{2} + yH_{2}O \rightarrow C_{x}SH_{y} + (3 x)CaCO_{3} \quad (1)$ $C_{2}S + (2 x)CO_{2} + yH_{2}O \rightarrow C_{x}SH_{y} + (2 x)CaCO_{3} \quad (2)$

These reactions are characterized by accelerated setting and rapid strength gain [1, 2].

In addition, concrete products such as bricks and blocks are subjected to high temperatures or steam curing in the plant to secure the initial strength, when energy is consumed and therefore CO_2 emissions are released. If the curing process that consumes energy during manufacturing of the concrete products is reduced, and the strength is secured by using the carbonation reaction, reduction in CO_2 emissions as well as storage of CO_2 can be achieved at the same time.

In this regard, studies on how to use CO_2 in the initial curing of the concrete product using CO_2 reaction in the initial stage was in progress [3-5], and basic research to confirm the CO_2 curing possibilities of cement products was also conducted in Korea [6].

In addition, industrial by-products such as flay ash and blasted furnace slag have been used as mineral admixtures for quality improvement and reductions in the amount of cement for the concrete products. However, as these admixture materials replace the cement and therefore sslow down the hydration reaction [7], the reaction cannot be activated until the initial three weeks due to the pozzolan reaction [8]. Later, C-S-H is additionally formed, while consuming Ca(OH)₂, a product of the cement hydration reaction, which poses a problem that promotes the carbonation by reducing the amount of Ca(OH)₂ reacted with CO₂ [9, 10]. This indicates that the CO₂ storage capacity decreases in concrete products made using admixture materials. However, it is

^{*}Corresponding author: Tel:+82-31-9112689

Fax: +82-31-9112689

E-mail: mcljc@naver.com

expected that if the carbonation is applied in the early stages of forming the concrete products that use admixture materials where hydration reaction does not occur, it is possible to increase the initial strength and store CO₂.

This study seeks to develop a CO_2 reduction-type concrete product that reduces the amount of cement by using industrial by-products such as fly ash and blast furnace slag, stores CO_2 and uses energy at the same time by applying CO_2 curing, and therefore can reduce the existing high-temperature curing time. Towards this end, the CO_2 uptake rate and initial strength improvement effects according to the mixing ratio of the admixtures and CO_2 curing were identified, and the CO_2 curing applicability of the concrete products made using admixture materials was investigated through a comparison of the existing steam curing, CO_2 uptake rate and compressive strength of 28 days.

Experimental

Materials

The materials used in this study include cement suitable for KS L 5201, ground granulated blast furnace slag corresponding to three kinds of KS F 2563, fly ash applicable to one kind of KS L 5405 as a substitute for cement. For fine aggregate, sand suitable for KS F 2526 was used.

Test overview

Tests were conducted by dividing them into two categories. Test A for investigating the CO_2 uptake rate of CO_2 cured specimens and comparing the initial strengths of 3 hrs and three days with dry cured specimens; test B for investigating the CO_2 uptake rate of CO_2 and high-temperature cured specimens and comparing it to high-temperature cured specimens.

First, for test A specimens, a cubic specimen of $50 \times 50 \times 50$ mm was molded using a mold according to the formulation of Table 1 and then demolded after being kept for two hours at room temperature. CO₂ cured specimens were cured at a CO₂ concentration of more than 95% for an hour in a CO₂ chamber (Fig. 1) and subjected to dry curing for three days in a constant

Table 1. Mixing plan.



(a) Equipment schematic diagram



(b) Equipment photo Fig. 1. CO₂ curing equipment.

temperature & humidity chamber with 20 °C and RH 60%, together with non CO_2 cured specimens with the same formulation. For CO_2 cured specimens, the compressive strengths of three hours after CO_2 curing and three days after dry curing were measured, and as for non CO_2 cured specimens, the compressive strengths after three hours and three days were measured for a comparison.

For test B, specimens were fabricated in the same size and manner as in Test A according to the formulation of Table 1, and CO_2 cured specimens were cured at a CO_2 concentration of more than 95% for 2 hrs in a CO_2 chamber), and then cured in a constant temperature & humidity chamber with 20 °C and RH 60% for 7 and 28 days after being cured in a stem curing chamber with 60 °C and RH 100% for 4 hrs. Non CO_2 cured specimens were cured in a steam

	Test specimens	W/C	FA	BS (%)	Unit weight(kg/m ³)				
		w/C	(%)		С	W	S	FA	BS
Test A	C30-30	30	0	0	300	90	2058	0	0
	C24F2-30	30	20	0	240	90	2036	60	0
	C24S2-30	30	0	20	240	90	2053	0	60
	C24F1S1-30	30	10	10	240	90	2044	30	30
Test B	C30-35	35	0	0	300	105	2020	0	0
	C24F1S1-35	35	10	10	240	105	2006	30	30
	C24F1S1-40	40	10	10	240	120	1967	30	30

curing chamber with 60 $^{\circ}$ C and RH 100% for 6 hrs, and then cured in a constant temperature and humidity chamber with 20 $^{\circ}$ C and RH 60% for 7 days and 28 days.

CO₂ uptake rate measurements

For CO_2 uptake rate measurements, the method of using changes in weight measured in real time at one-minute intervals with the use of electronic scales in a CO_2 curing process, and the method of using differences in thermal gravity by the composition of CO_2 with the use of thermogravimetric analysis (TGA) was used in this study.

First, real-time CO_2 uptake rate measurements using electronic scales (GF 6100, AND, Japan) were conducted according to Equation (3) modified by the expression proposed by El-Hassan et al [11].

$$CO_2 uptake(\%) = \frac{M_c - A_m + E_m}{C_m} \times 100$$
(3)

wherein, M_c : weight change of specimen during CO₂curing (g)

 A_m : weight change of air in a chamber during CO₂curing (g)

 E_m : natural water evaporation loss of specimen under a curing condition in a chamber without CO₂ (g)

 C_m : amount of cement used for specimen (g)

In addition, the amount of cement used in the specimen was calculated according to Equation (4).

$$C_m(g) = MN_c \times \frac{C_c}{C_c + W_c + S_c} \tag{4}$$

wherein, MN_c : specimen weight before CO₂curing (g)

 C_c : cesment content per unit volume of concrete (kg/m³)

 W_c : water content per unit volume of concrete (kg/m³)

 S_c : weight of fine aggregate per unit volume of concrete (kg/m³)

In CO₂ cured specimens, CaCO₃ is produced by carbonation reactions, and the CaCO₃ is known to be decomposed into CaO and CO₂ at heating temperatures ranging from 550 to 950 °C [12]. Therefore, TGA is a method of analyzing the components using changes in the thermal gravity of specimens according to the heating temperature, and thus it can analyze CO₂ weight by the weight difference when heated up to 1,000 °C. In this study, the thermal gravity was measured using DSC-TGA (SDT Q600, TA Instrument, USA).

Also, for the CO_2 uptake rate estimation method using TGA, a calculation was conducted using Equation (5) modified from the expression proposed by El-Hassan et al [11].

$$CO_2 \ uptake(\%) = \left(\frac{C_{550} - C_{1000}}{C_m} - \frac{MC_{550} - NC_{1000}}{NC_m}\right) \times 100$$
(5)

wherein, C_{550} : thermal gravity of CO₂ cured specimen

at 550 °C (g)

 C_{1000} : thermal gravity of CO₂ cured specimen at 1000 °C (g)

 C_m : cement weight of CO₂cured specimen (g)

 NC_{550} : thermal gravity of non CO₂ cured specimen at 50 °C (g)

 NC_{1000} : thermal gravity of non CO₂ cured specimen at 1000 °C (g)

 NC_m : cement weight of non CO₂cured specimen (g)

Since the sample for TGA is obtained from the cured specimen, it is mixed with cement and sand. Accordingly, there is a need to calculate the amount of cement contained in the sample. The cement amount of the sample is calculated as the ratio of cement to the sum of the cement content per unit volume of concrete and weight of fine aggregate per unit volume of concrete in the sample under absolutely dry conditions at 550 °C as shown in Equation (6). However, in order to meet the absolutely dry conditions of the sample, the weight of fine aggregate per unit volume of concrete was calculated by applying an absolutely dry weight ratio of 98.22% obtained from subtracting the absorption rate.

$$C_m(NC_m)(g) = C_{550}(NC_{550}) \times \frac{C_c}{C_c + 0.9822 \times S_c}$$
(6)

Phenolphthalein spray test

Phenolphthalein is commonly used as a pH indicator. It turns red in alkaline conditions and shows no change in color in neutral ones. Therefore, it can be easily identified as there is no change in color when carbonation is made.

Compressive strength test

In order to analyze the strength characteristics according to curing methods and the strength characteristics according to the use of admixture materials, the compressive strengths at 7-and 28-day ages were tested according to KS L 5105, "Compressive Strength Test Method of Hydraulic Cement Mortar".

Results and Discussion

CO₂ uptake rate and carbonation

The results obtained by the weight change measurement method using an electronic scale in the CO_2 curing process of being carbonated to CO_2 with a concentration of 95% for an hour showed that the CO_2 uptake mass increased until the initial 15 minutes, but then it decreased slightly and maintained a constant value about 30 minutes later (Fig. 2). Therefore, the mean value in 30 minutes after the CO_2 measurement was calculated as the CO_2 uptake mass, and the CO_2 uptake rate and cement amount calculated according to Equation 3 and Equation 4 were summarized in Table 2. According to the results, the CO_2 uptake rate ranged



Fig. 2. CO_2 uptake mass result by electronic scale.

Table 2. CO₂ uptake rate by electronic scale.

Specimens	Binder mass (g)	CO ₂ uptake mass (g)	CO ₂ uptake rate (%)
C30-30	25.63	1.98	7.73
C24F2-30	25.91	2.00	7.73
C24S2-30	25.70	1.54	6.01
C24F1S1-30	26.61	1.54	5.79

from 5.79 to 7.73%, and the uptake rate of the specimen mixed with blast furnace slag was found to be slightly low.

Table 4. Calculated real CO_2 uptake rate of specimens with admixture by TGA.

Specimens	C30-30	C24F2-30	C24S2-30	C24F1S1-30
CO ₂ uptake rate (%)	4.57	6.75	8.37	4.22

For calculation of the CO_2 uptake of specimens by TGA, the CO_2 uptake rate, cement amount and TGA specimens weight before and after CO_2 curing calculated using Equation 5 and Equation 6 were shown in Table 3. Then the real CO_2 uptake rate of specimens calculated using the preceding results were summarized in Table 4. The CO_2 uptake rate of specimens by TGA ranged from 4.22 to 8.37%, which leads to a difference of 0.3%p when compared with the specimen not mixed with admixture materials, showing similar or more than 2% higher tendencies.

In comparison with the measurement method using the electronic scale, the CO_2 uptake rate calculation method using TGA is adjudged to have a variation since the size of the sample is small, but it showed the results, where the CO_2 uptake rate of specimens mixed with each 10% of fly ash and blast furnace slag was lowest, identically.

Fig. 3 shows the phenolphthalein spray results of the



C30-30

C24F2-30 C24S2-30

C24F1S1-30

Fig. 3. Phenolphthalein spray results of the CO₂ cured specimen and the non CO₂ cured specimen (3 hours after forming).

Table 3. Mass and CO_2 uptake rate of specimens with admixture to	by T	GA
--	------	----

Specimens		Initial mass (g)	Mass at 550 °C (g)	Mass at 1000 °c (g)	Mass of Binder (g)	CO ₂ uptake rate (%)
	C30-30	45.21	44.70	43.43	16.59	7.70
CO ₂ cured	C24F2-30	25.46	25.26	24.32	9.41	9.99
specimen	C24S2-30	26.95	26.66	25.57	9.90	11.00
	C24F1S1-30	36.02	36.02	35.02	13.42	7.45
	C30-30	51.60	50.56	49.96	18.93	3.14
CO ₂ cured	C24F2-30	44.84	44.05	43.51	16.57	3.24
specimen	C24S2-30	51.89	51.18	50.68	19.07	2.63
	C24F1S1-30	42.43	41.66	41.15	15.64	3.23



Fig. 4. Early compressive strength of specimens by CO₂ curing.

 CO_2 cured specimen (3 hours after forming) and non CO_2 cured specimen. While the non CO2cured specimen turned red as it became alkaline due to the production of Ca(OH)₂through a hydration reaction, the CO₂ cured specimen was found to exhibit little change in color and was subjected to carbonation inside as the hydration reaction was not properly made. However, the C30-30 specimens appear to look a little redder than other specimens mixed with admixture materials, which is due to a slight hydration reaction.

Compressive strengths

As shown in Fig. 4, the compressive strength of the non CO₂ cured specimen mneasured after 3 hrs ranged from 0.04 to 0.08 N/mm², and from 0.89 to 1.15 N/ mm²after 3 days. On the other hand, the compressive strength of the CO₂ cured specimen was 2.31-2.85 N/ mm² in two hours after forming and immediately after CO₂curing for an hour, and it was $4.01 \sim 4.79 \text{ N/mm}^2$ at the age of 3 days, which confirms that CO_2 curing is effective in the early strength development. In addition, the compressive strength of the CO₂ cured specimens was highest in the specimen not mixed with admixture materials, followed by the specimen mixed with 10% fly ash and blast furnace slag, the specimen mixed with 20% blast furnace slag, and the specimen mixed with 20% fly ash, indicating that the mixing of fly ash and blast furnace slag by 10% is effective in terms of the strength development.

Jin-O Park, Jong-Chan Lee, Sae-Hyun Lee



Fig. 5. CO₂ uptake mass by electronic scale.

Table 5. CO₂ uptake rate by mass change.

Specimens	Binder mass (g)	CO ₂ uptake mass (g)	CO ₂ uptake rate (%)
C30-35	29.21	2.66	9.10
C24SF-35	29.15	2.70	9.26
C24SF-40	29.55	2.46	8.31

CO₂ uptake rate and carbonation

Fig. 5 shows the CO₂ uptake mass measured in real time using an electronic scale in the CO₂ curing process of being carbonated to CO₂ with a concentration of 95% for 2 hrs. Of these measurement values, the mean values for an hour after an hour with few variations were presented in Table 5. The CO₂ uptake rate according to admixture materials and W/C differences was 8.31-9.26 % and was the highest in the specimen mixed with 10% each of fly ash and blast furnace slag, W/C 30%.

The results of the CO₂ uptake rate analysis using TGA were summarized in Tables 6 and 7. The results revealed that the specimen with 10% each of fly ash and blast furnace slag, W/C 40% provided the highest rate of 18.64%, followed by the specimen with 10% each of fly ash and blast furnace slag, W/C 35% (12.6%), and the specimen with no admixture materials, W/C 35% (11.09%), which showed a different tendency from that of the method using an electronic scale. However, since TGA methods may yield different result values depending

Speci	mens	Initial mass (g)	Mass at 550 °C (g)	Mass at 1000 °C (g)	Mass of Binder (g)	CO ₂ uptake rate (%)
	C30-35	43.06	41.68	40.42	5.48	23.06
CO ₂ curing	C24SF-35	43.32	42.19	40.96	5.58	22.03
	C24SF-40	54.59	53.18	51.34	7.15	25.69
Non	C30-35	39.76	37.86	37.26	4.97	11.97
CO_2	C24SF-35	41.67	39.80	39.15	5.26	12.38
curing	C24SF-40	44.25	41.81	41.21	5.62	10.75

Table 6. Mass of specimens with admixture by TGA.

Table 7. Calculated CO_2 uptake rate of specimens with admixture by TGA.



Fig. 6. TGA result of CO₂ cured specimens.



Fig. 7. TGA result of non CO₂ cured specimens.

on samples, each 10% of fly ash and blast furnace slag, W/C 35% formulation is found to have a positive effect on the CO_2 uptake rate, given that the results of the CO_2 uptake rate measured using an electronic scale are also taken into account.

Figs. 6 and 7 show the TGA results of specimens subjected to CO_2 curing for two hours and non CO_2 cured specimens after the same time. For CO_2 cured specimens, only CaCO₃, which is a product of carbonation reactions, was identified, and the non CO_2 cured specimen was found to have a hydration product Ca(OH)₂ and a carbonation reaction product CaCO₃. The reason why CaCO₃ is detected even in non CO_2 cured specimens is considered to be due to the sample carbonation caused by CO_2 in the air during the process of TGA test, which should be subtracted in the CO_2 uptake rate measurements by TGA.

Compressive strengths

As shown in Fig. 8, the compressive strength of the CO_2 cured specimen was 9.56-10.48 N/mm² at the age of 7 days, and 12.25-14.10 N/mm² at the age of 28 days. For the non CO_2 cured specimen, the compressive strength ranged from 8.71 to 10.47 N/mm² at 7 days, and ranged from 12.17 to 13.88 N/mm² at 28 days,



Fig. 8. Compressive strength of specimens with admixture.



Fig. 9. Compressive strength ratio of CO_2 cured specimens to non CO_2 cured specimens.

showing that the compressive strength in the early 7 days of CO_2 curing was slightly higher, but became similar at 28 days. This suggests that the compressive strength of the early 7 days is due to the effect of the CO_2 curing on the strength development, and that of the 28 days is attributed to the 4-hour steam curing implemented after CO_2 curing. In other words, since the non CO_2 cured specimen was subjected to steam curing for 8 hours, 2-hr CO_2 curing is assumed to provide the same strength development effect as that of 4-hr steam curing.

Fig. 9 shows the compressive strength development ratio of CO_2 cured specimens to non CO_2 cured specimens, which exhibits a generally positive effect of CO_2 curing on the strength development. In particular, as CO_2 curing is verified to be helpful in increasing the strength in both C24SF-35 and C24SF-40 specimens, the applicability of CO_2 curing techniques to cementitious products made using admixture materials can also be confirmed.

Conclusions

This study was conducted to analyze the effects of concrete products made using fly ash and blast furnace slag as admixture materials on CO_2 uptake rates and compressive strengths in CO_2 curing. Based on the results, the following conclusions were drawn.

According to the first test results, if an admixture of

20% compared to the cement weight was used, regardless of the type of admixture material, the CO_2 uptake rate was found to be 2% lower when compared to the case when the admixture was not added. CO_2 curing also turned out to be very effective in increasing the early compressive strength. However, the strength of the specimen mixed with the admixture was slightly lower than that of the specimen to which the admixture was not added even though CO_2 curing was conducted.

The second test results showed that if 10% each of fly ash and blast furnace slag were used, and W/C was more than 35%, the CO₂ uptake rate was found to be similar when compared to the case when the admixture materials were not added, and especially the case of W/C 35% turned out to be superior, regardless of the CO₂ absorption rate measuring method. Even in terms of increasing the compressive strength, CO₂ curing of two hours was found to exhibit a similar strength development effect to steam curing of 4 hrs.

Therefore, it is expected that if concrete products are produced through the formulation of W/C 35% and 10% each of fly ash and blast furnace slag, the application of CO_2 curing and steam curing in combination can contribute to ensuring the equivalent strengths and reducing CO_2 .

References

- C.J. Goodbrake, J.F. Young, R.L. Berger, J. Am. Ceram. Soc. 78 [11] (1979) 2867-2872.
- J.F. Young, R.L. Berger, J. Breese, J. Am. Ceram. Soc. 57
 [9] (1974) 394-397.
- H. El-Hassan, Y. Shao, Mag. Conc. Res. 66 [14] (2014) 708-718.
- S.K. Haghighi, S. Ghoshal, Ind. Eng. Chem. Res. 52 [16] (2013) 5529-5537.
- 5. C. Shi, F. He, Y. Wu, Constr. Build. Mater. 26 [1] (2012) 257-267.
- J.C. Lee, J. Archit. Inst. Korea Struct. Constr. Sect. 31 [8] (2015) 43-50.
- A. Younsi, ph. Turcry, A. Ait- Mokhatar, S. StanquetCem. Concr. Res. 43 (2013) 25-33.
- 8. X.Y. Wang, H.S. Lee, onstr. Build. Mater. 23 [2] (2009) 725-733.
- P. Sulapha, S.F. Wong, T.H. Wee, S. Swaddiwuddhipong, J. Mater. Civ. Eng. 15 [2] (2003) 134-143.
- K. Sisomphon, L. Franke, Cem. Concr. Res. 37 [12] (2007) 1647-163.
- H. El-Hassan, Y. Shao, Z. Ghouleh, ACI Mater. J. 110 [4] (2013) 441-450.
- 12. J.S. Kwack, C.S. Kang, H.S. Lee, Inst. Korea Struct. Constr. Sect. 28 [7] (2012) 125-132.