Study on quantification of CO₂ absorption of hardened cement for concrete using CCU materials

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Abstract. Towards a carbon-neutral society, in the concrete sector, in addition to considering the use of large amounts of additions to reduce the amount of cement, CO2 fixation technologies using carbonation reactions are also being considered. Considering a sustainable society, the use of recycled aggregates is also an important topic, as is the production of concrete using CO₂-captured aggregates. Furthermore, if the CO₂ absorption of the constructed structure can be quantified, it is possible to link this to the carbon footprint of the constructing structures. Therefore, in this study, an attempt was made to quantify the CO₂ absorption of cement replaced with ground granulated blast furnace slag in units of cement paste. Here, the relationship between the degree of hydration and the amount of CO2 absorption was investigated, assuming that the CO2 absorption of hydration products in the hardened cement paste is large. As a result, it was found that hydration progressed with extended curing, and that the amount of CO2 absorbed was greater when hydration progressed, and a high correlation was observed between the amount of CaO that became hydrate as a result of hydration progression and the amount of CO₂ absorbed. By applying this, it was confirmed that the CO₂ absorption in the paste section in recycled aggregate can be increased.

Keywords: Carbonation, CO₂ absorption, Ground Granulated blast furnace slag, Hydration reaction

1 Introduction

In recent years, rising sea levels, droughts and extreme weather events caused by global warming have been occurring, and efforts are being made worldwide to solve the global warming problem. Japan has also declared that it will achieve carbon neutrality by 2050, the zero emissions of greenhouse gases that cause global warming and is considering the creation of a decarbonised society in a variety of fields. The concrete industry is also actively working on this issue [1]. Among them, the property of concrete to absorb carbon dioxide (CO_2) by utilizing its carbonation reaction is attracting attention. Concrete has long been known to undergo carbonation degradation, in which highly alkaline concrete reacts with CO_2 in the air to reduce its alkalinity and approach

neutrality, resulting in corrosion of reinforcing bars. This reaction is a reaction that produces calcium carbonate by reacting with CO_2 (carbonation reaction) according to the chemical formulas represented by Equations (1) and (2), indicating that hardened cement materials such as concrete have the property of absorbing and fixing CO_2 in the hardened samples.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$	(1)
$3CaO \cdot SiO_2 \cdot 3H_2O + CO_2 \rightarrow 3CaCO_3 + 2SiO_2 + 3H_2O$	(2)

It is also known that cement, which is a concrete constituent, emits a large amount of CO_2 during the production of clinker, the raw material for cement, and although the use of cement mixed with addition materials such as ground granulated blast furnace slag and fly ash is expected to reduce the amount of CO_2 emitted from binder, the use of cement with such addition materials is expected to reduce the amount of CO_2 emitted from binder, the use of cement with such addition materials is expected to reduce the amount of CO_2 emitted from clinker, however CO_2 absorption when these addition materials are used has not been studied in many cases.

Factors influencing the carbonation of concrete include the type and replacement ratio of the addition material, water-cement ratio, shape and size of the specimen and curing environment as conditions for the hardened samples [2][3]. Furthermore, environmental conditions for carbonation may include temperature and humidity, CO_2 concentration, carbonation period, and carbonation methods such as dry or wet. As such, various factors can be considered to influence carbonation, and it is considered necessary to organise the effects of various conditions on CO_2 absorption and quantify CO_2 absorption in order to calculate the carbon footprint. This study focused on the degree of hydration of carbonated samples and organised the effects on the unit absorption capacity of CO_2 in formulations with different replacement rates of ground granulated blast furnace slag. In concrete structures, the ease of CO_2 penetration in the depth direction is considered to influence the CO_2 absorption capacity. By using thick specimens, the CO_2 absorption capacity, which includes the ease of CO_2 penetration, was investigated.

2 Assessment of the potential for CO₂ absorption

2.1 Materials used and test specimen specifications

In this study, Ordinary Portland Cement (OPC) and Ground Granulated Blast Furnace Slag 4000 (without gypsum, GGBS) were used, with anhydrite gypsum added to GGBS at an internal rate of 2% SO₃ equivalent. As a basic experiment to assess the CO₂ absorption potential of hardened cement, the study was conducted on cement paste specimens to eliminate the influence of aggregates. The mix proportions are shown in Table 1. The cements were OPC, OPC with 30% substitution of GGBS for BA, BB with 50% substitution and BC with 70% substitution. And also calculated the amount of CaO in cement paste samples. After wetting, the specimens were hand-kneaded for 2 min in a constant temperature and humidity chamber at 20°C and 60% RH, stirred

every hour to account for bleeding effects, and used after 6 h. The specimens were cast in 40 x 48 mm zippered plastic bags with 4 g of each sample to produce a specimen of about 1.5 mm thickness.

	W/B	W/B Replacement of	Unit weight (kg/m ³)			Amount of
	(%)	(%) GGBS (%)	Water	OPC	GGBS	(%)
N50	50	0	612	1225	0	43.4
BA50		30	606	849	364	39.1
BB50		50	602	602	602	36.2
BC50		70	598	359	837	33.4

Table 1. Mix proportion for cement paste samples

2.2 Carbonation conditions

The prepared cement pastes were sealed and cured (20° C) in zippered plastic bags for a specified period as 1,3,7,28,56 days. In order to eliminate the influence of CO₂ permeability, the specimens were ground using a mill after demoulding to produce a powdered form. Carbonation was carried out for 7 and 28 days at a temperature of 20° C, a relative humidity of 60% RH and a CO₂ concentration of 20%. In this process, 70% of water was added by dipping water to the mass of the sample before carbonation, as previous studies [4] have reported the importance of the presence of water for the dissolution of CO₂ in the reaction field during the carbonation reaction. Curing periods of 1, 3, 7, 28 and 56 days were used to vary the degree of hydration. After carbonation, the samples were pulverised with a large amount of acetone to stop hydration.

2.3 Determination of calcium carbonate and calculation of CO₂ absorption

Differential thermogravimetric analysis (TG-DTA) was performed on samples for measuring the amount of CO₂ absorption of each sample on different hydration ratio. Measuring conditions were from room temperature to 1000°C, with a temperature increase rate of 20°C/min and an N₂ flow environment. The calcium hydrate and calcium carbonate content were calculated each from the mass loss about 450 °C and between 550 and 850 °C, as the inflection point of the DTA curve peak was unclear in some cases; the mass loss relative to the mass before heating at 1000 °C was calculated as the calcination content, and the difference before and after carbonation as the CO₂ absorption content. The amount of calcium hydroxide was calculated from the mass loss between the inflection points of the peaks of the DTA curve. The amount of calcium hydroxide and calcium carbonate in the sample weight before measurement was quantified to calculate the amount of CO₂ absorption, since the aim here was to quantify the amount of CO₂ in the hardened samples.

2.4 Results of testing

(1) CO₂ absorption for different curing periods

Fig.1 shows the relationship between the curing period and CO_2 absorption for different GGBS replacement rates. As a general trend, it was found that the amount of CO_2 absorption increased as the curing period lengthened. It is considered that the increase in hydration of cement clinker and GGBS due to the extension of the curing period is the reason for the increase in hydrates. This figure also shows that the amount of CO_2 absorption decreased as the replacement ratio of GGBS increased. This is considered to be due to the small amount of CaO contained in the powder in blends with high substitution rates.



Fig. 1. Results of CO₂ absorption ratio for curing periods on different cement types

(2) CO_2 absorption with different carbonation periods

The results of CO_2 absorption for samples cured for 7 days and carbonated for 7 and 28 days are shown in Fig.2. The CO_2 absorption derived from the carbonation of calcium hydroxide is separated from the decrease in calcium hydroxide before and after carbonation. The CO_2 absorption increased slightly with increasing carbonation period. However, the increase was small, and under the carbonation conditions in this study, carbonation for more than 7 days is considered to have little effect on the duration of the carbonation period according to the previous study, but Fig.2 shows that in N50, about 1/2 of the CO_2 absorption came from the carbonation of calcium hydroxide, whereas in BC50 it was about 1/5. This is thought to be due to a decrease in the amount of calcium hydroxide produced by the hydration of OPCs as the amount of OPC decreases.

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Fig. 2. Amount of CO₂ absorption on different hydration products

(3) Relationship between the amount of CaO in the hydrated sample and the amount of CO_2 absorption

The estimated maximum value of CO_2 absorption was calculated assuming that all the CaO content in the samples reacted with CO_2 through carbonation. The CO_2 absorption rate obtained from the results of TG-DTA against the estimated value was calculated as the CO_2 absorption rate. The results of the CO_2 absorption rate for N50, BA50, BB50 and BC50 at 7 days of carbonation are shown in Fig.3. The CO_2 absorption did not reach 100% during the curing period of any of the samples, because of the hydrates that are present in a form that does not contribute to the absorption of CO_2 . The absorption is lower as the substitution ratio increases. It was also observed that the CO_2 absorption rate tended to increase as the curing period increased. It is suggested that CaO in the mix proportion is more likely to contribute to CO_2 absorption as hydration progresses.



Fig. 3. CO2 absorption per calculated CO2 absorption from CaO on different mix proportions

3 Relationship between hydration ratio and CO₂ absorption

As indicated in the previous chapter, it is clear that an increase in the curing period increases the amount of CO_2 absorption. This is thought to indicate that the extension of curing, in short, the progress of the hydration reaction, increases the amount of CO_2 absorption due to an increase in the hydration products. The amount of CaO contained in the hydration products was estimated from the reaction rates of OPC and GGBS, and the relationship between the amount of CaO and the amount of CO_2 absorption was summarised.

3.1 Measurement of reaction rates

(1) Reaction rate of OPC

Samples that had been hydrated stopped by immersing the sample in a large amount of acetone to avoid carbonation and drying were used to measure the reaction rate of OPCs. Powder X-ray diffraction measurements were carried out by D2 PHASER (BrukerAXS). Corundum (α -Al₂O₃) was added to the sample as an internal standard at an internal ratio of 10%. The measurement conditions for powder X-ray diffraction were X-ray source Cu-K α , tube voltage 30 kV, tube current 10 mA, search range $2\theta = 5-60^{\circ}$, step width 0.025° and scan speed 0.025°/min. For analysis, multiple peak separation was performed using the WFFP method with the software TOPAS 4.2 to separate adjacent or overlapping peaks; the OPC reaction rate was calculated as the sum of the reaction rates of the four clinker minerals, using the peak positions and integrated intensities calculated with reference to previous studies [5][6]. The integrated intensity (wavefront area) of the diffraction lines at the peaks of the separated 4 clinker minerals was calculated. From using an internal standard method, the integral intensity of the minerals relative to corundum was used as the integral intensity ratio.

(2) Reaction rate of GGBS

The selective dissolution method with salicylic acid, acetone and methanol solution was used to determine the reaction rate of blast furnace slag. Hydration was stopped by immersing the sample in a large amount of acetone to avoid carbonation and drying it. The sample was added to a salicylic acid, acetone and methanol solution, stirred for 1 hour and allowed to stand for 23 hours, and the unreacted slag was determined from the insoluble residues. The reaction rate of the slag was calculated [7]. The unreacted residues from OPC were corrected to 0.211 from the literature [7] because the unwanted residues include the aluminate phase derived from OPC and the pore phase of the ferrite phase.

3.2 **Results of degree of hydration**

The amount of CaO in the hydration products was calculated using results of degree of hydration. The amount of CaO in hydrates at N50, BA50, BB50 and BC50 is shown in Fig.4. Regardless of the mix proportions, the amount of CaO in the hydrates increased with increasing curing period. After 7 days of curing, the increase in CaO content was

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slow, indicating that the reaction progressed slowly. It was also observed that the CaO content decreased as the GGBS replacement ratio increased. On the other hand, no significant differences were observed in the relationship between the different curing periods, suggesting that the reaction generally progresses in the same way in different mix proportions.

The relationship between the amount of CaO and CO₂ absorption of hydrates is shown in Fig.5. As an overall trend, it has a good relationship with the amount of CO₂ absorption increasing as the amount of CaO in the hydrate increases. This suggests that the amount of CO₂ absorption increases with increasing hydrates.

In the carbonation reaction to produce calcium carbonate, CaO and CO₂ can be considered to react at 1:1. The line where the amount of CaO in the hydrate and the amount of CO₂ absorbed are 1:1 is shown in Fig. 5; the smaller the GGBS replacement ratio, the greater the deviation from 1:1, suggesting that even CaO present in the hydrate is unlikely to contribute to CO₂ absorption. From previous studies [8], it is known that the Ca/Si ratio is smaller in the GGBS-substituted hardened specimens than when OPCs are used, suggesting the influence of different Ca/Si ratios and the fact that the C-S-H in the specimens is not fully carbonated.



Fig. 4. Amount of CaO in hydration products on different cement type and curing periods



Fig. 5. Relationship between Amount of CaO and CO₂ absorptions

4 Conclusions

The results obtained in this study are as follows.

(1) When carbonation of specimens of the same age was carried out in the same environment, the results showed that CO_2 absorption was greater at lower GGBS replacement rates. The CO_2 absorption of powder samples with different curing periods showed that the CO_2 absorption increased as the curing period increased.

(2) From the above, a positive correlation between the amount of CO_2 absorption and the amount of CaO in the hydrates was confirmed, and it was inferred that the CaO in the sample exists as a form that easily contributes to carbonation through the hydration reaction.

By applying these results, the recycled aggregates such as attached mortar's carbonation, can be expected to result in high CO_2 absorption conditions.

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