

Experimental study on quantification of carbon dioxide adsorption by different cement types and mix proportions

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ABSTRACT: Efforts are underway in concrete to build a carbon dioxide-free society. The degree of CO₂ adsorption and fixation by hardened cement, concrete depend on the type of cement and water-binder ratio of the hardened cement. In this study, we analyzed various types of hardened cement by TG-DTA to determine the amount of CO₂ adsorbed and examined the possibility of quantifying the amount of CO₂ adsorbed by weight increase as a simple method. As a result, it was shown that the amount of adsorption differs depending on the type of cement, that water is necessary for CO₂ adsorption mechanism, and that the amount of adsorption can be determined simply by the weight change.

1 INTRODUCTION

The global effort to move away from carbon dioxide has a significant impact on the concrete industry. The manufacture of cement, one of the raw materials for concrete, emits enormous amounts of carbon dioxide, which must be curbed. Therefore, in addition to cement production using energy-saving technologies as much as possible, technologies to use large quantities of alternative cement materials with low carbon dioxide emissions are being developed worldwide. On the other hand, concrete has long been known to undergo carbonation and is said to absorb carbon dioxide during service. This is believed to lead to a decrease in the small amount of carbon dioxide in the atmosphere. For carbon dioxide to be adsorbed and immobilized as calcium carbonate, a large amount of calcium is required in the concrete. On the other hand, a factor that increases the depth of carbonation is thought to be the use of cement with more admixture or a higher water-cement ratio to penetrate carbon dioxide deeper into the concrete. Furthermore, it has been pointed out that the presence of water is important for the carbonation phenomenon.

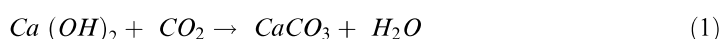
Therefore, the purpose of this study was to compile data that would contribute to the quantification of the amount of carbon dioxide fixed by carbonation of hardened cement. Specifically, we quantified the amount of calcium carbonate produced when environmental conditions and water content were varied in order to sort out the effects of water content in the reaction field. Furthermore, the amount of calcium carbonate produced was determined by changing the total amount of calcium by varying various cement types and water-cement ratios. In addition, the amount of calcium carbonate produced was investigated by adjusting the pores so that carbon dioxide gas could enter deep into the specimens. Furthermore, we attempted to quantify the amount of calcium carbonate produced by changing the weight of the sample so that the ratio of calcium carbonate produced could be easily measured.

2 OVERVIEW OF EXPERIMENTS

2.1 *Changes in hydrates and voids due to carbonation*

Carbonation of cement hydrates results in carbonation of the hydrates as shown in the chemical equation below. In this process, it is considered that the increase in volume due to the binding of carbon dioxide and the dissipation of the water produced occur simultaneously.

As indicated in the literature, it is also pointed out that carbonation of calcium hydroxide may result in densification of pores due to the formation of calcite, while carbonation of CSH may result in coarsening or opening of pores with the collapse of CSH as well as the formation of vaterite. Especially in cements containing a large amount of blast furnace slag powder, the change in porosity is known to be significant, suggesting that it also affects the progression of carbonation depth.



2.2 *Preparation for the test*

To organize how much carbon dioxide is adsorbed and immobilized by various types of hardened cement, it can be imagined that there are influencing factors such as the test environment (temperature and humidity, carbonation gas concentration), carbonation period, carbonation in air (dry) and in water (wet) as test conditions, as shown in Figure 1. Also, the type of cement (calcium content), water-cement ratio, and specimen size (shape) can be considered as influencing factors in the mixing conditions of the hardened specimens. We quantified the amount of carbon dioxide fixation by using samples with these factors.

In preparing the specimens, the powders used were ordinary Portland cement (Density 3.16 g/cm³) and blast furnace slag fine powder (Density 2.91 g/cm³). Three types of cement were prepared: OPC, B50 (50% replacement of blast furnace slag fine powder), and B70 (70% replacement of blast furnace slag fine powder), with a water binder ratio of 0.5.

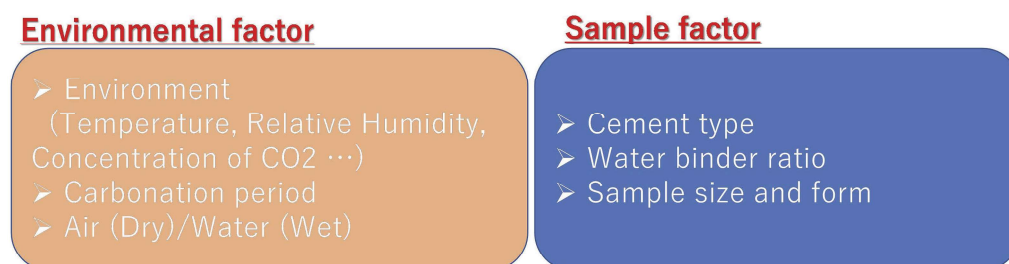


Figure 1. Influencing factor for absorption of Carbon dioxide.

For the determination of carbon dioxide adsorption, (1) the amount of calcium carbonate and calcium hydroxide were determined using TG-DTA, and (2) the amount of carbon dioxide adsorption by weight increase was determined. Because it was considered that the measurement of weight change would be difficult if affected by moisture absorption or moisture transpiration before and after carbonation, the samples were stored in a humidity-controlled environment using a desiccator so that the temperature and humidity were the same as those in the carbonated environment, as shown in Figure 2.

After 7 days of sealing and curing, the prepared specimens were placed in a humidity-controlled environment (20°C, 60% R.H.) for 21 days until there was no change in mass after the specimens were shaped. The specimens were then accelerated carbonated in a carbonation environment (20°C, 60% R.H., 5% carbon dioxide concentration) for 7, 14, 21, and 28 days, and the changes were measured by the methods described in TG-DTA and weight change.

(1) Determination of calcium hydroxide and calcium carbonate by TG-DTA

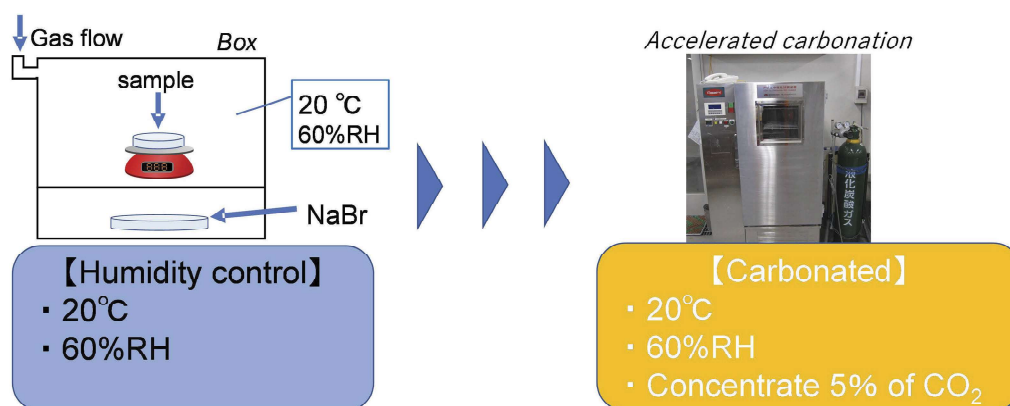


Figure 2. Weight change for determining the CO₂ absorption by easily methods.

The temperature range was 20 to 1000°C, and the rate of temperature increase was 10°C / min. The amount of dehydration of calcium hydroxide (CH) and calcium carbonate (CaCO₃) was estimated from the inflection point of the DTA curve and calculated from the decrease in weight change with endothermic peak. Tests were conducted under a nitrogen gas environment to eliminate the effects of oxidation and carbonation during the measurement.

(2) Determination of absorb carbon dioxide easily by Weight change

To quantify the amount of carbon dioxide adsorbed, the mass change was measured using an electronic balance capable of measuring down to 0.1 mg. After measuring the mass of the specimens after humidity conditioning was completed, mass measurements were taken for each carbonation material age, and the amount of carbon dioxide adsorbed was calculated from their differences.

3 RESULTS OF CARBON DIOXIDE ABSORPTION

3.1 Effects of cement type, carbonation period, and specimen shape

(1) Outline

The specific surface area of the specimen was examined for possible effects of the surface in contact with carbon dioxide and the voids in the hardened sample. As a sample, a fixed amount of cement paste was poured into a 38 x 40 x 2 mm zippered plastic bag, and the bag was sealed and cured for 7 days. After that, as shown in Figure 3, a “hardened” specimen and a “powder” specimen were prepared by grinding the specimen to less than 150 μm using a grinding mill.

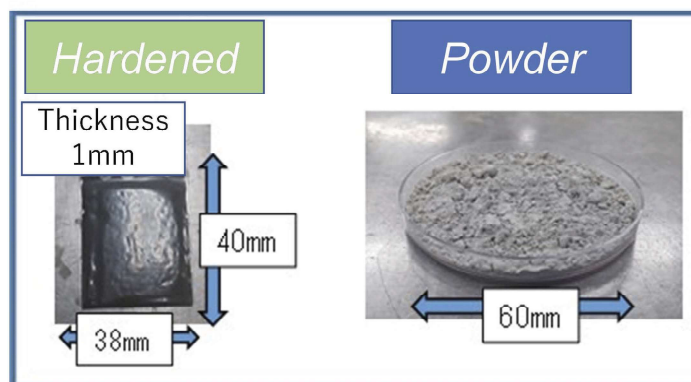


Figure 3. Sample size and form.

(2) Results

Figure 4 shows the percentage of CaCO_3 content in the samples calculated by TG. The results are organized by different cement and specimen geometries. In addition, the total CaCO_3 content derived from CH were separated. Based on the amount of CH calculated from the sample prior to carbonation, the difference between the amount of CH remaining during each carbonation period was calculated as the lost CH turned into CaCO_3 . It was also assumed that the total amount of CaCO_3 minus the amount of CH-derived CaCO_3 was produced by the carbonation of CSH and aluminate hydrates.

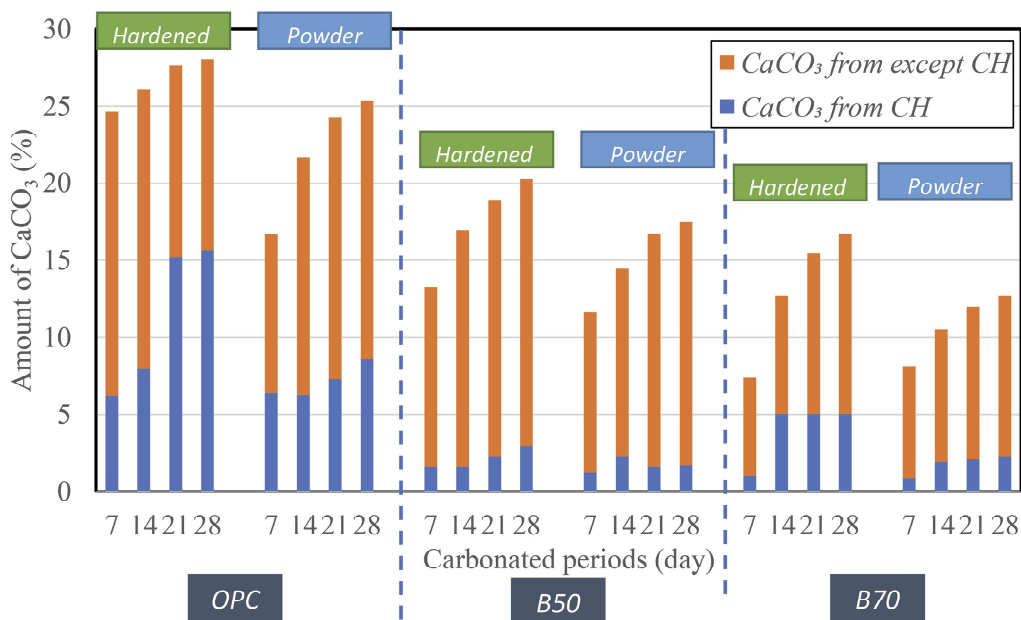


Figure 4. Amount of CaCO_3 by different cement type and sample forms.

From these results, the first comparison of cement types shows that OPC produces the most CaCO_3 , followed by B50 and B70. This means that the amount of CO_2 absorption decreases as more blast furnace slag fine powder is substituted. In addition, the effect of each carbonation period shows that the amount of CaCO_3 gradually increases, but the increase in adsorption after 14 days is not large. The subsequent examination of the specimen forms shows that for all cement types, the “hardened” specimens have a higher amount of CaCO_3 than the “powder” specimens. Initially, it was assumed that more CO_2 adsorption would occur in the powder with a larger specific surface area, but the results were different. In addition, when the origin of CaCO_3 production was compared, the amount of CH-derived CaCO_3 production was estimated to be lower when “powder” was used. Naturally, it is understandable that the addition of blast furnace slag fine powder to the cement type reduces the amount of CH, and therefore the amount is reduced, but the following study should be conducted to determine the reason for the smaller amount of “powder”.

3.2 Moisture content during carbonation

(1) Outline

The results verified in 3.1 showed that the “powder” with a larger specific surface area produced less CaCO_3 than the “hardened” specimen. Considering that the reaction of carbonation takes place through moisture, we thought that this might be because the powder almost lost its liquid phase, whereas the “hardened” could create a liquid phase even at 60% RH in the micro-porosity. In other words, we think that it may be extremely difficult for CH to become CaCO_3 if the moisture content of the sample is low. Therefore, we decided to test the “powder” and

humidity-controlled samples by adding water to the samples prior to carbonation. The Figure 5 shows the amount of water added to the samples. A fixed amount of water was added to the powdered sample to create an excess of water before accelerated carbonation was performed.



Figure 5. Moisture contents during carbonation.

(2) Results

Figure 6 shows the amount of CaCO₃ after carbonation for samples with 0, 30, 50, and 70% moisture addition. The amount of CaCO₃ derived from CH and from other sources as same as Figure 4, respectively. Even though the cement types are different, the amount of CaCO₃ is higher for those with more water added. The amount of CaCO₃ derived from CH also increased significantly. On the other hand, the amount of CaCO₃ derived from other sources did not increase that much. In addition, the carbonation periods were 3, 5, and 7 days, and although the amount of CaCO₃ gradually increased, no significant changes were observed. This indicates that the larger the moisture content in the sample, the more carbonation of CH is likely to occur, indicating that the presence of moisture is important. It is also clear that the carbonation of powder does not progress most rapidly at 60% RH.

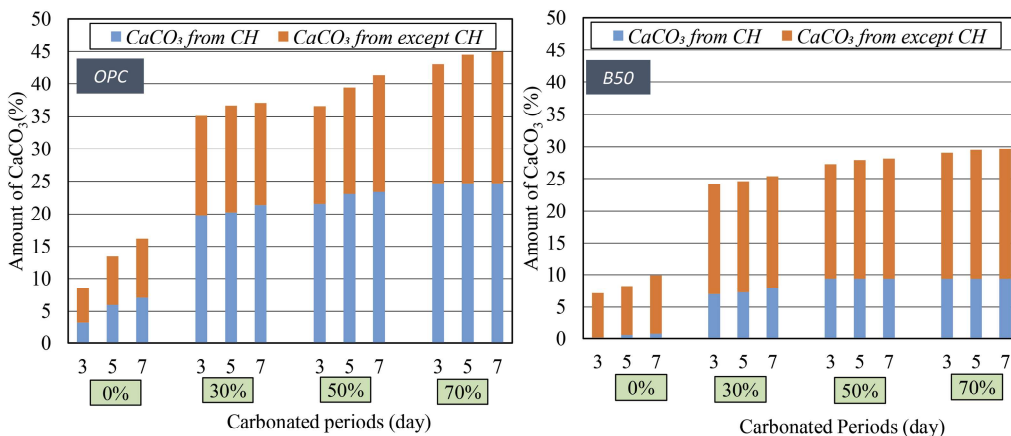


Figure 6. Amount of CaCO₃ by different of water contents.

3.3 Effect of cement type and water binder ratio

(1) Outline

To consider that the amount of CO₂ adsorption by carbonation depends on CaO, the effects of cement type and water binder ratio were varied. OPC and GGBFS cements were used, with replacement ratios of 30, 50, and 70%. Cement pastes were prepared by changing the water-binder ratio to 0.3, 0.5, and 0.7, respectively. The prepared samples were the same as those used in 3.1 and were ground before conditioning. Water was added to 70% of the sample mass just before carbonation to clarify the CO₂ adsorption potential of the hardened product, since water content has a significant effect as obtained in 3.2. The accelerated carbonation conditions were the same as in 3.1, and the number of days of carbonation was measured at 3 and 7 days. The items measured were TG-DTA and mass measurement.

(2) Results

Figure 7 shows the amount of CaCO_3 produced at each cement and water binder ratio, separated into those from CH and those from other sources. Although there was some variation in the data for each cement, it was observed that the cement with a low water-binder ratio of 0.3 tended to adsorb more CO_2 and produce more CaCO_3 . On the other hand, when looking at CH-derived CaCO_3 , the higher water-binder ratio produces more CaCO_3 . This is thought to be because of water content.

Figure 8 further shows the relationship between the amount of CaO and the amount of CaCO_3 produced. The higher the amount of CaO in the cement paste, the more CaCO_3 is produced, and the more CO_2 is adsorbed.

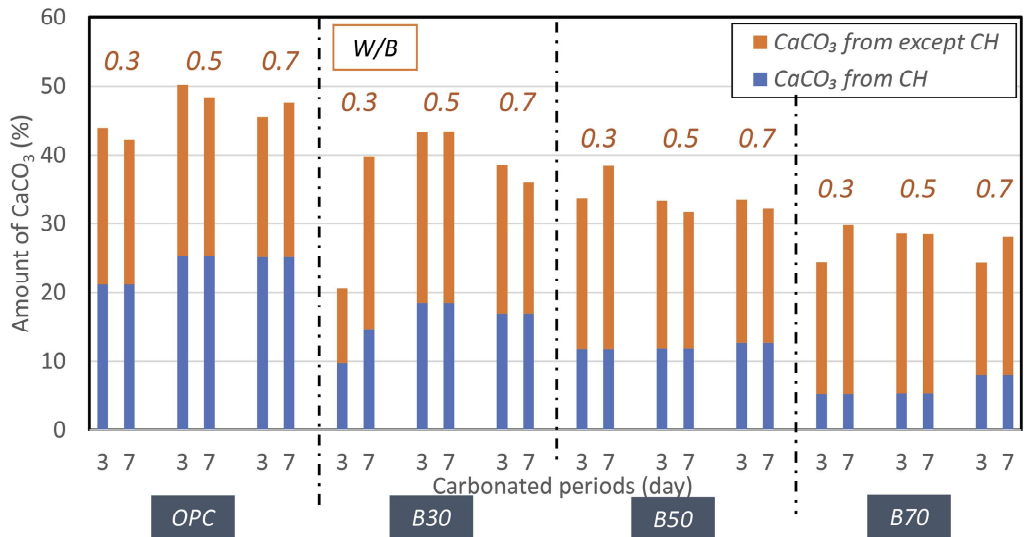


Figure 7. Amount of CaCO_3 by different water binder ratio.

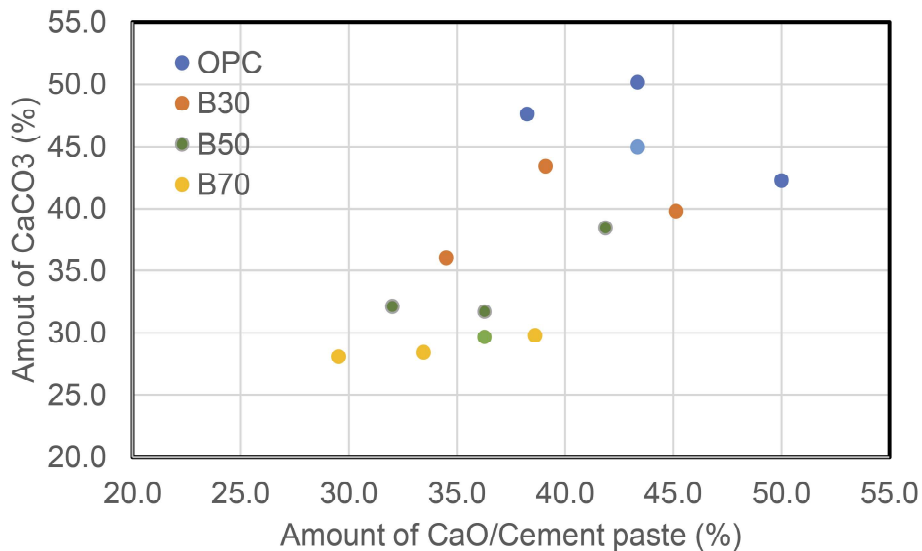


Figure 8. Relationship between the Amount of CaO and CaCO_3 .

3.4 Relationship between weight change and the amount of CO₂ capture

Figure 9 shows the relationship between the measured weight change and the amount of CO₂ adsorption determined from TG. All results are included for cement type, carbonated periods, specimen shape, and moisture adjustment performed in 3.1, 3.2 and 3.3. There is generally a positive correlation between the rate of weight change and the amount of CO₂ adsorption, and that a proportional relationship is also nominated. The higher the replacement ratio of blast furnace slag, the smaller the weight change and CO₂ adsorption, and the larger the weight change and CO₂ adsorption are for OPC alone. The effect of the addition of moisture is greater in the case of the sample with additional moisture. This indicates that the CO₂ adsorption amount of cement paste can be estimated by determining the weight change before and after carbonation, although the accuracy needs to be examined in the future.

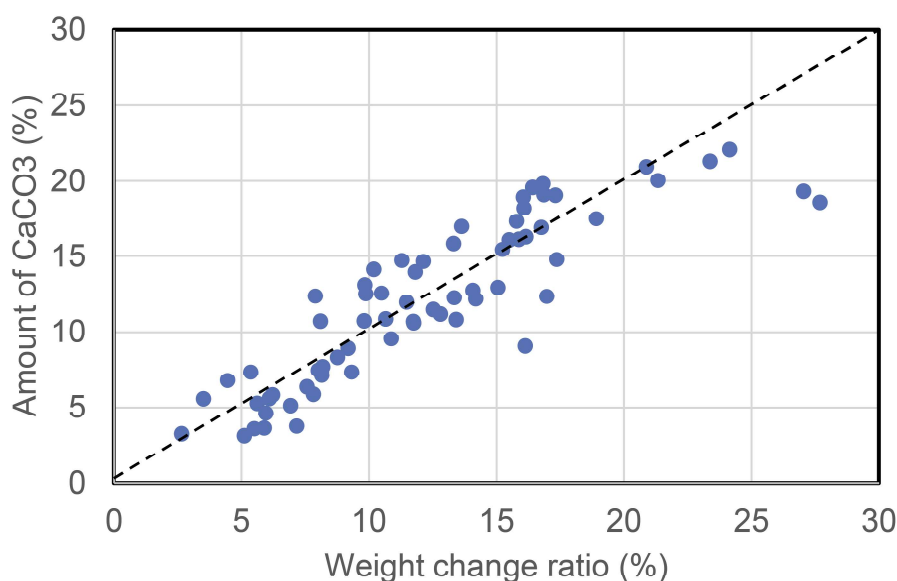


Figure 9. Relationship between the weight change and CO₂ absorption ratio.

4 CONCLUSIONS

The results obtained from this study are summarized as follows.

- (1) The CO₂ adsorption potentials of different cement types tended to be highly dependent on the calcium content of the cement.
- (2) In carbonation, carbonation reaction proceeds at 60%RH in hardened cements because water can be retained in the capillary pores, but in powders, carbonation of CH is less likely to proceed because of the lack of water retention.
- (3) It is possible to estimate the amount of CO₂ adsorbed from the weight change of a cement paste sample under humidity-controlled conditions and a sample after carbonation.

In the future, we will investigate the relationship in the water-binder ratio and aim to quantify the amount of CO₂ adsorption by weight change in mortar and concrete blocks containing aggregate.

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