

## Evaluation Methods of Concrete Carbonation Suppressive Performance of Surface Coating

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### ABSTRACT

Various studies have been conducted to estimate the ability of coating materials to suppress the carbonation process in concrete. The typical method for determining the effect is to use an accelerated carbonation test of concrete specimens with various coating materials. After the accelerated carbonation test, the neutralization depth is usually determined by using phenolphthalein. In our study, thermogravimetric analysis (TGA) was also performed besides using the phenolphthalein method in order to evaluate the carbonation suppressive performance more quantitatively. Next, in order to develop a method for the evaluation of the suppressive effect that is quicker than the accelerated carbonation test, we developed a box method that we could apply to evaluate the carbon dioxide (CO<sub>2</sub>) permeability of a variety of coating materials. The main results obtained can be summarized as follows:

- 1) It is well known that a parabolic law can be obtained between carbonation periods and neutralization depth values determined by the phenolphthalein method. It has been confirmed that such a parabolic law can also be obtained between carbonation periods and the total amounts of CaCO<sub>3</sub> formed in the specimens. The coefficients of the neutralization rate obtained from both of the parabolic relations reasonably correspond to each other.
- 2) The box method can quickly evaluate the carbon dioxide permeability and is useful for predicting the effect that coating materials have on the suppression of the carbonation process in concrete.

**Keywords.** Carbonation Suppressive Performance, Accelerated Carbonation Test, Thermogravimetric Analysis, Carbon Dioxide Permeability, Box Method.

### INTRODUCTION

A suppression of neutralization (carbonation) is expected for finishing materials applied to reinforced concrete. Such a suppression effect can be evaluated by an outdoor exposure test, an accelerated neutralization test, an investigation of the actual buildings, etc. The degree of neutralization is usually evaluated by determining the neutralization depth by spraying the concrete with a phenolphthalein solution.

The neutralization of concrete is a phenomenon where calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), produced by the hydration reaction of cement changes to calcium carbonate ( $\text{CaCO}_3$ ) by reacting with carbon dioxide in air. Therefore, it is necessary to quantitatively examine the distribution of  $\text{CaCO}_3$  produced and the total amount of  $\text{CaCO}_3$ .

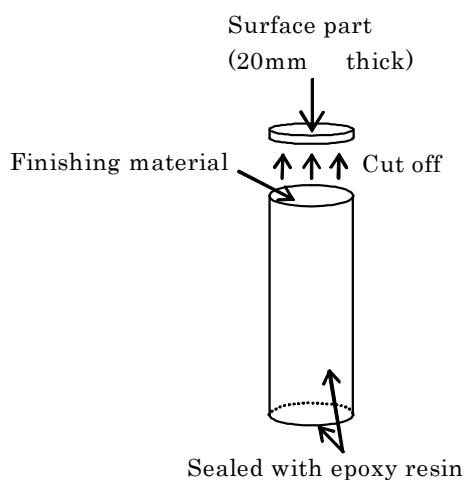
The ability of various types of finishing materials to suppress neutralization was evaluated from the viewpoint mentioned above by applying an accelerated neutralization test to evaluate specimens with mortar base substrates. Additionally, the thermogravimetric analysis (TGA) method was used to evaluate the degree of neutralization of the mortar, with which the amount of  $\text{CaCO}_3$  was estimated quantitatively. The neutralization depth was also determined by the phenolphthalein method, and this was compared with the results of the quantitative analysis of  $\text{CaCO}_3$ .

There are a wide variety of coating materials in the market, and their carbonation suppressing effects are different. However, the suppression effect of each coating product has not been quantified enough because it takes a long time to perform the accelerated carbonation test. In order to evaluate the suppression effect of each coating product, it is useful to develop a rapid and simple method, compared with the accelerated carbonation test, which requires waiting some months before obtaining results.

A new rapid and simple method is proposed in this paper. The carbon dioxide ( $\text{CO}_2$ ) permeation rate for coating materials was evaluated using a box test method that was developed by modifying the box test method used for the evaluation of the water vapor transmission rate of coating materials.

## EXPERIMENTAL METHOD

**Mortar specimens.** Cylindrical test specimens, 100 mm in diameter and 400 mm in height, were made of cement mortar, prepared as shown in Table 1. The mortar test specimens were aged with a wet compress and water spray for the first two weeks and then kept at  $20 \pm 2^\circ\text{C}$  and  $\text{RH } 65 \pm 5\%$  for the next two weeks. To completely avoid a laitance layer appearing on the cast mortar surface, the part from the surface to a depth of 20 mm was cut off using a concrete cutter, as shown in Figure 1. The surface, on which the finishing materials were to be applied, was polished with an abrasive paper with a grain size of P180 (prescribed by the Japanese Standards Association [JIS R 6252:2006])



**Figure 1. Mortar test specimen.**

**Table 1. Materials and mix proportion.**

	Materials and mix proportion
Cement	Ordinary portland cement (Specified in JIS R 5210:2009)
Fine aggregate	River sand, Absolute dry specific gravity 2.56, Water absorption 2.22%
Cement / Sand	1:2.8
Water cement ratio	60% (45% and 75% in some specimens)

Mortar test specimens were prepared with the finishing materials shown in Table 2. The application specifications of the finishing materials were based on the standard specifications from the material manufacturers. Epoxy resin was also carefully applied twice to the side and bottom surfaces of the specimens so that the coating thickness was 1 mm.

**Table 2. List of surface-finishing materials.**

Code No.	W/C (%)	Surface-finishing material
1-1	75	None (Bare mortar)
1-2	60	None (Bare mortar)
1-3	45	None (Bare mortar)
2	60	Polymer-modified cement mortar (SBR latex, Polymer Loading 5%, 10mm thick)
3	60	Polymer-modified cement mortar (SBR latex, Polymer Loading 14%, 10mm thick)
4	60	Polymer-modified cement mortar (SBR latex, Polymer Loading 20%, 10mm thick)
5	60	Epoxy resin mortar (5mm thick)
6	60	Epoxy resin mortar (10mm thick)
7	60	Acrylic emulsion paint (2 coats)
8	60	Polyurethane paint (2 component type, 1 coat)
9	60	Polyurethane paint (2 component type, 2 coats)
10	60	Acrylic paint (Solvent type, 2coats)
11-1	75	Multilayer textured emulsion coating (Water proofing type)
11-2	60	Multilayer textured emulsion coating (Water proofing type)
11-3	45	Multilayer textured emulsion coating (Water proofing type)
12	60	Thin textured emulsion coating (Water proofing type)
13	60	Multilayer textured emulsion coating (Ordinary type)
14-1	75	Thin textured emulsion coating (Ordinary type)
14-2	60	Thin textured emulsion coating (Ordinary type)
14-3	45	Thin textured emulsion coating (Ordinary type)
15-1	75	Water-repellent material (Silane compound)
15-2	60	Water-repellent material (Silane compound)
15-3	45	Water-repellent material (Silane compound)
16	60	Water-repellent material (Acrylic resin)

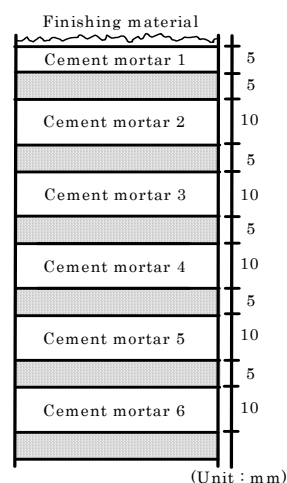
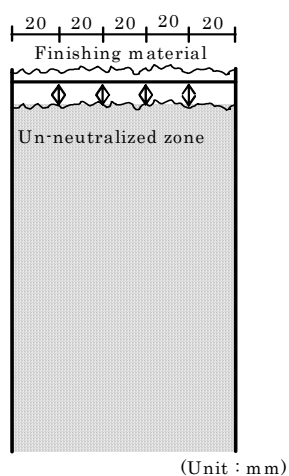
**Accelerated neutralization.** After the application of finishing materials, the mortar test specimens were aged at room temperature for one month. Then, accelerated neutralization processing was performed at a temperature of 30°C at RH 60%, and a CO<sub>2</sub> concentration of 2%, for 6 or 24 months.

**Measurement of neutralization depth and quantitative determination of CaCO<sub>3</sub> with the TGA method.** The mortar test specimens, to which the 6- or 24-month accelerated neutralization processing had been applied, were cut into two parts. With one part, the neutralization depth was determined with the phenolphthalein method. No neutralization regions were observed on the side and bottom surfaces that had been sealed by epoxy resin, and therefore, the average of the depth of the four parts indicated in Figure 2 was used as the neutralization depth of each mortar test specimen.

Next, the other part was further cut off using a finishing cutter, as shown in Figure 3. The 5-mm thick gray sections shown in Figure 3 are the tab for the cutter. Moreover, the mortar test specimens were cleaved to get to the central parts, which were disintegrated using a ball mill or a mortar.

Scanning thermogravimetric analysis equipment (TGD-3000, Shinkuriko Co., Ltd.) was used for the TGA. Mortar powder samples of approximately 45 mg were weighed exactly using a

quartz cell. The TGA was performed by heating the samples starting at room temperature and increasing their temperature at a rate of 5°C/min until the samples reached 1000°C.

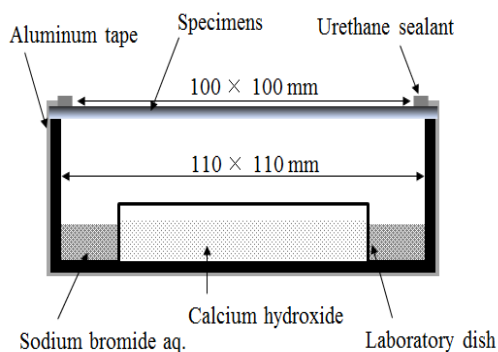


**Figure 2. Measurement of neutralization depth.** **Figure 3. Cutting of cement mortar specimens.**

**Table 3. List of surface-finishing materials.**

Code	Surface coating materials
S1	Thin textured emulsion coating (Ordinary type, 1.28 mm thick)
S2	Thin textured emulsion coating (Ordinary type, 1.11 mm thick)
S3	Thin textured emulsion coating (Ordinary type, 0.48 mm thick)
FS	Thin textured emulsion coating (Water-proofing type, 1.16 mm thick)
ES	Thin textured emulsion coating (Water-proofing type, 0.57 mm thick)
AT	Multilayer textured emulsion coating (Ordinary type, 0.76 mm thick)
FT	Multilayer textured polymer-modified cementitious coating (Water proofing type, 1.13 mm thick)
ET	Multilayer textured emulsion coating (Water proofing type, 0.88 mm thick)
EP	Acrylic emulsion paint (0.23 mm thick)
EP-E	Flexible acrylic emulsion paint (0.22 mm thick)
EP-G	Acrylic emulsion glossy paint (0.23 mm thick)

**Coating materials evaluated with the box method.** Table 3 shows the coating materials evaluated with the box method. Each coating material was painted on coarse filter paper to obtain a coating film. Each painted filter paper was conditioned for two weeks at 23°C and 60% RH to allow for a film to completely form.



**Figure 4. Box method.**

**Table 4. Humidity conditioning materials.**

Conditioning Material	RH. (%)*
Water	100
Saturated solution of ammonium chloride	79.2
Saturated solution of sodium bromide	59.1
Saturated solution of magnesium chloride	33.1
Powder of calcium chloride	0

\*at a temperature of 20°C

**Evaluation of CO<sub>2</sub> permeability with the box method.** CO<sub>2</sub> permeability was measured by using a test box shown in Figure 4. The following steps were performed:

- 1) The box was made of welded vinyl-chloride resin plates, and it had inner dimensions of 110 × 110 mm. The box was covered with aluminum tape to enhance airtightness.
- 2) To remove the influence of moisture that is produced by the carbonation reaction, a humidity conditioning material was placed in the box. For example, 40 ml of a saturated aqueous solution of sodium bromide was placed in the box, which resulted in relative humidity of approximately 60%. The other conditioning materials used to create other relative humidity conditions are shown in Table 4.
- 3) Ca(OH)<sub>2</sub> reagents as specified by the Japanese Standards Association [JIS K 8575] were placed uniformly in a laboratory dish with a diameter of 90 mm. The amounts of Ca(OH)<sub>2</sub> used were 4, 8, 20, and 25 g.
- 4) The coating film specimens including paper filters were attached to the upper side of the box using a urethane sealant.

The test box was placed under the conditions of 20°C, 60% RH, and a CO<sub>2</sub> concentration of 5%. After the carbonation period, the laboratory dish was removed from the test box. The Ca(OH)<sub>2</sub> in the laboratory dish was dissolved in water. Then, phenolphthalein reagent was added to the solution. The residual Ca(OH)<sub>2</sub> was titrated by 0.1 mol/l acetic acid. The amount of CaCO<sub>3</sub> that was produced was calculated on the basis of the amount of Ca(OH)<sub>2</sub> that was consumed.

## RESULTS AND DISCUSSION

**Estimation of CaCO<sub>3</sub> contents from thermogravimetric curves.** An example of TGA curves is shown in Figure 5. The TGA curves for all the mortar specimens greatly decrease at around 100°C, as shown in Figure 1. Such a decrease in mass is considered to be due to the evaporation of the water contained in the specimens. Also, at temperatures above 200°C, each curve shows a stable base line after the completion of water evaporation.

Each TGA curve shows a great decrease in the mass of the surface part (cement mortar 1) of the mortar test specimen at temperatures below and above 600°C. Such a decrease in mass might be due to the thermal degradation of CaCO<sub>3</sub> produced in the mortar, as shown in Eq. 1, from which the CaCO<sub>3</sub> contents were estimated.

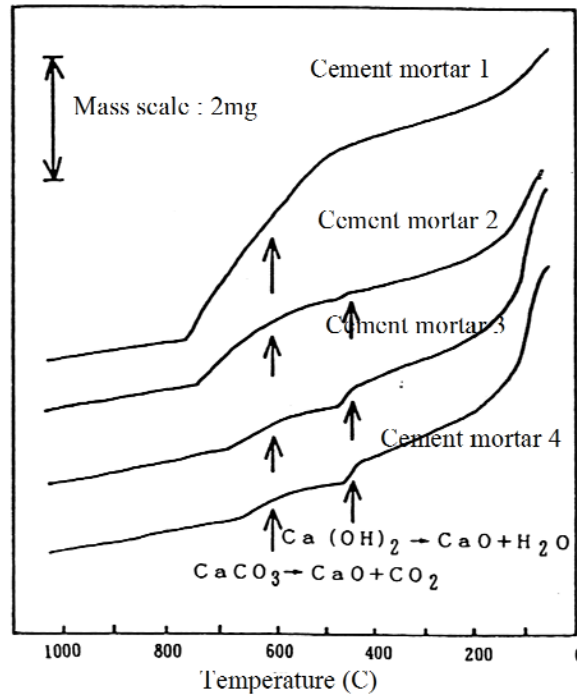


In addition, as clearly seen from the comparison of the thermogravimetric curves of cement mortars 1, 2, 3, and 4, for example, as the depth recedes from the finishing surface, the decrease in mass observed around 600°C decreases owing to the degradation of CaCO<sub>3</sub> and the decrease in mass observed around 400°C increases. The decrease in mass around 400°C is expected to be due to the dehydration reaction of Ca(OH)<sub>2</sub>, as shown in Eq. 2, from which the contents of Ca(OH)<sub>2</sub> can be quantitatively estimated.



Thus, the following observations were made from Figure 5.

- 1) Ca(OH)<sub>2</sub> does not exist in cement mortar 1 because of the neutralization.



**Figure 5. An example of TGA curves (cement mortar without coating, W/C 75%, and 6 months of accelerated carbonation).**

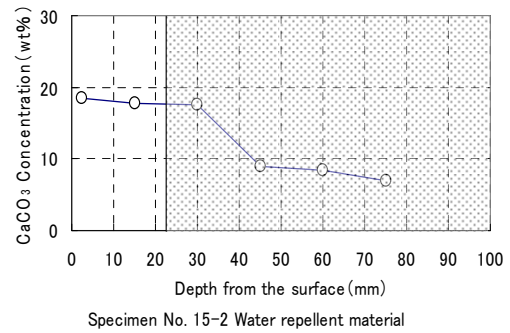
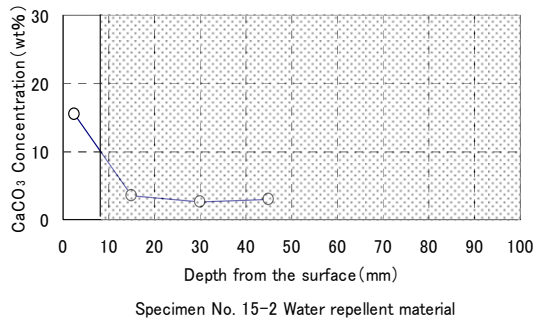
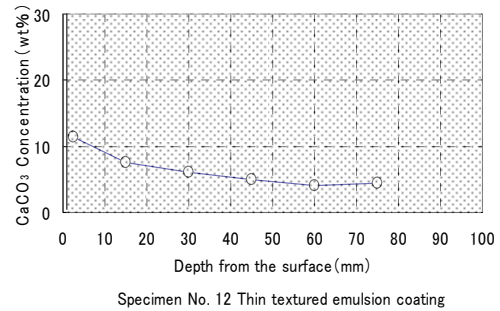
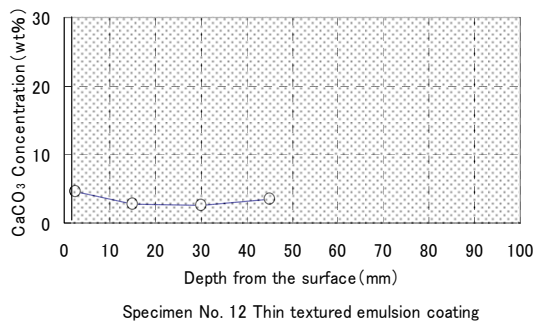
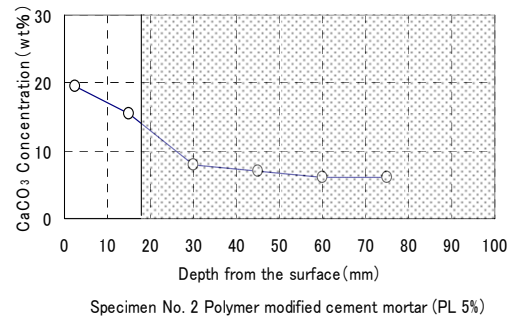
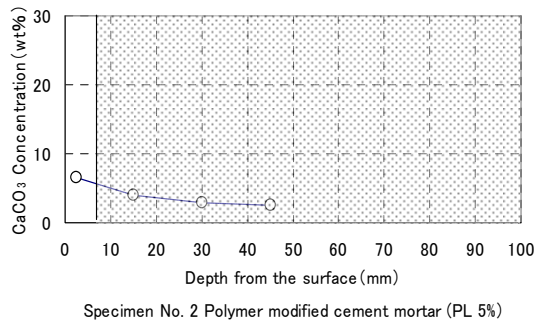
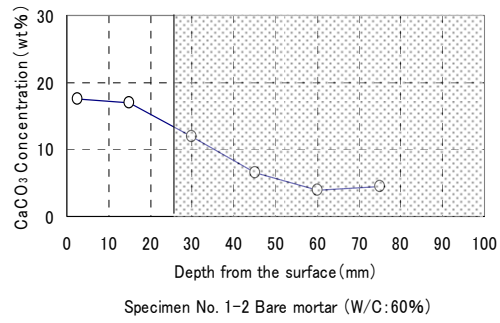
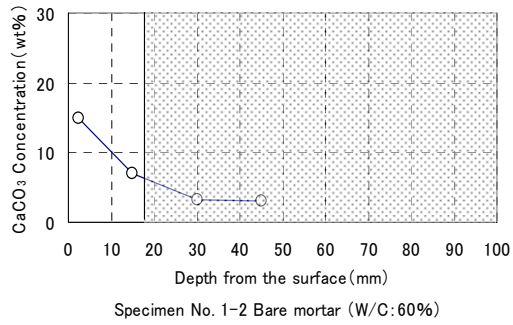
- 2) On the other hand, in cement mortar 4, far from the surface, there is a large amount of  $\text{Ca(OH)}_2$  and a small amount of  $\text{CaCO}_3$ , because the neutralization progresses very little.
- 3) For cement mortars 2 and 3, the amounts exhibited values between those of cement mortar 1 and 4. Also, the idea that the decreases in mass around 600°C and 400°C might be caused by the decreases in  $\text{CaCO}_3$  and  $\text{Ca(OH)}_2$ , respectively, was confirmed by additionally performing the TGA of  $\text{CaCO}_3$  [JIS K 8617:1996] and  $\text{Ca(OH)}_2$  [JIS K 8575:1994] under the same conditions. At the same time, the TGA of fine aggregates was performed, and no  $\text{CaCO}_3$  and  $\text{Ca(OH)}_2$  was confirmed.

From the TGA curves obtained, the amounts of  $\text{CaCO}_3$  and  $\text{Ca(OH)}_2$  were quantitatively estimated. The amounts of  $\text{CaCO}_3$  are discussed in this paper.

#### **Estimation of concentration gradient and integrated amount of $\text{CaCO}_3$ in mortar test specimens.**

Figure 6 shows the in-depth concentration gradients of  $\text{CaCO}_3$  for the six-month accelerated neutralization processing test specimens. Figure 7 shows the results of the 24-month accelerated neutralization processing test specimens. As can be seen in Figure 6, neutralization does not reach the deep region of the 6-month processing test specimens.

Therefore, for the 6-month neutralization processing mortar specimens, the TGA tests were performed on the sections from mortar 1 to mortar 4 (which were located at a region 40–50 mm from the surface, as shown in Figure 3). However, for mortar test specimens 1-1, because only a small amount of  $\text{CaCO}_3$  was observed, as shown in Figure 5, and TGA tests were performed on the sections from mortar 1 to 5.



**Figure 6. Concentration gradients of CaCO<sub>3</sub>. (6 month newtralization)**

**Figure 7. Concentration gradients of CaCO<sub>3</sub>. (24 month newtralization)**

Also, the amount of CaCO<sub>3</sub> for each mortar test specimen is indicated at each depth from the surface, on the basis of the cutting pattern of the mortar test specimens, as shown in Fig. 3. For example, for mortar 1, the amount of CaCO<sub>3</sub> at a depth of 2.5 mm is shown, and for mortar 2, the amount of CaCO<sub>3</sub> at a depth of 15 mm is shown. The amounts of CaCO<sub>3</sub> are expressed by their ratio to the absolute dry mass of mortar (dried at 110°C for 24 h) as a percentage.

As clearly shown in Figures 6 and 7, for mortar test specimens in which neutralization has progressed, the amount of  $\text{CaCO}_3$  gradually decreases as the depth increases from the surface. Moreover, it was found that  $\text{CaCO}_3$  exists in the un-neutralized region determined by the phenolphthalein method and that  $\text{Ca}(\text{OH})_2$  exists in the neutralization region.

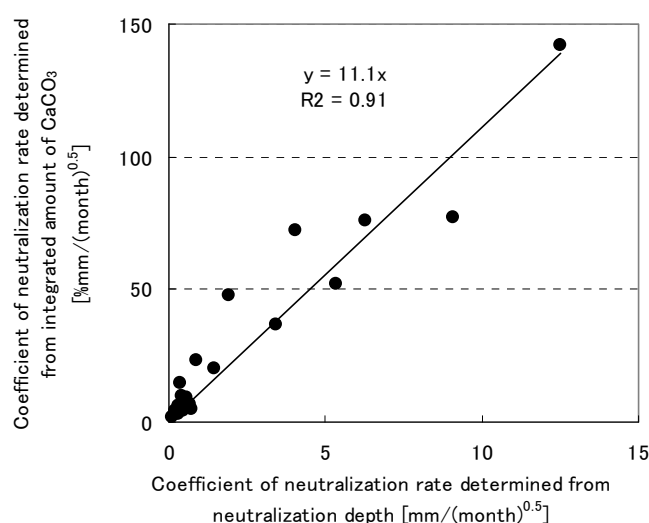
Also, Figures 6 and 7 show that a large percentage of  $\text{CaCO}_3$  exists even in the deep region far from the surface, which was expected not to be neutralized. This can be considered to be an error induced by the sloping of the base line of the TGA curves. Therefore, in the estimation of the integrated amount of  $\text{CaCO}_3$ , if the  $\text{CaCO}_3$  contents show a certain low value in the deep region, the  $\text{CaCO}_3$  contents in the region were compensated to be zero.

This integrated amount of  $\text{CaCO}_3$  indicates a measure of the total amount of  $\text{CaCO}_3$  produced in the accelerated neutralization processing of the mortar test specimens, corresponding to the areas of the shaded parts in the curves of Figs. 6 and 7. The integrated amounts of  $\text{CaCO}_3$  were determined by adding the all-shaded parts of the graph.

Figures 6 and 7 clearly show that the  $\text{CaCO}_3$  content apparently increases up to approximately 20% during the process of neutralization. However, as previously mentioned, when the  $\text{CaCO}_3$  content in the un-neutralized region was corrected to make it zero, the  $\text{CaCO}_3$  content in the neutralization-completed region was 12% at a maximum.

According to Kasai [1983], the mass of  $\text{Ca}(\text{OH})_2$  produced by the hydration of standard Portland cement is considered theoretically to be 25–29% of the hardened substances produced. In this study, because the cement-aggregate mass ratio is 1:2.8, the mass fraction of  $\text{Ca}(\text{OH})_2$  in whole mortar is 6.6–7.6%. Moreover, considering the mass increment when the entire amount of  $\text{Ca}(\text{OH})_2$  (74g/mol) changes to  $\text{CaCO}_3$  (100g/mol) by complete neutralization, the content of  $\text{CaCO}_3$  in the mortar can be estimated to be 9–10%. The 9–10%  $\text{CaCO}_3$  content estimated theoretically compares closely with the compensated  $\text{CaCO}_3$  content, 12% at a maximum as previously mentioned, although it is a little bit larger.

**The relationship between the neutralization depth determined by the phenolphthalein method and the amount of integrated  $\text{CaCO}_3$  in mortar.** In general, the neutralization depth of concrete is formulated using Eq. 3.



**Figure 8. The relationship between the coefficients of neutralization rate determined from the neutralization depth and the integrated amounts of  $\text{CaCO}_3$ .**



$$C = A(t)^{0.5} \quad (3)$$

where C is the neutralization depth (mm), t is the time (month), and A is a coefficient of the neutralization rate estimated from the neutralization depth ((mm/(month)<sup>0.5</sup>). Assuming that the neutralization rate equation for the neutralization depth determined by the phenolphthalein method is also valid for the integrated amount of CaCO<sub>3</sub>, the following is obtained.

$$S = B(t)^{0.5} \quad (4)$$

where S is the integrated content of CaCO<sub>3</sub> (% mm), t is time (months), B is a neutralization rate coefficient estimated from the integrated content of CaCO<sub>3</sub> ((% mm/(month)<sup>0.5</sup>)).

Figure 8 shows the relationship between the neutralization rate coefficient determined from the neutralization depth and that from the integrated amount of CaCO<sub>3</sub>; both coefficients were found to be strongly correlated with each other, and the former coefficient was approximately 11 times the latter ( $Y = 11.1X$ ,  $R = 0.96$ ). That is, from such a relationship shown in Figure 8 and Eq. 4, the following equation can be derived,

$$S = 11.1 (\%) \times C \quad (5)$$

where S is the integrated amount of CaCO<sub>3</sub> (% mm), and C is the neutralization depth (mm).

As mentioned above, in the region where neutralization was expected to be completed, the CaCO<sub>3</sub> content was 12% in the mortar as determined from the thermogravimetric analysis. This value is consistent with the value of 10% estimated using the report from Kasai [1983]. In addition, Eq. 5 indicates that the integrated CaCO<sub>3</sub> content (% mm) can be obtained by multiplying the neutralization depth by a constant value of 11.1%. That is, when assuming that the CaCO<sub>3</sub> content is uniformly 11.1% in the neutralization region determined by the phenolphthalein method, and that CaCO<sub>3</sub> does not exist in the un-neutralized region, the total amount of estimated CaCO<sub>3</sub> was found to correspond well with the integrated amount of CaCO<sub>3</sub> determined by the thermogravimetric method. Moreover, the constant of 11.1% is close to the maximum value of CaCO<sub>3</sub> content of 12% in the surface region where neutralization was completed.

In other words, although the produced CaCO<sub>3</sub> is actually distributed with a concentration gradient in the mortar test specimens, the total amount of integrated CaCO<sub>3</sub> can be approximated by the amount of CaCO<sub>3</sub> calculated by assuming that the specimens are completely neutralized in the region above the neutralization depth determined by the phenolphthalein method and that they are not absolutely neutralized in the un-neutralized region.

**Evaluation of CO<sub>2</sub> permeability using the box method.** The relationship between time and the concentration of CaCO<sub>3</sub>, as determined by titration, is shown in Figure 9. The concentration of CaCO<sub>3</sub> proceeds almost linearly until it reaches a plateau at approximately 60% in Figure 9. It was found that the amount of generated CaCO<sub>3</sub> depends on the type of coating materials. This difference is due to the different permeability of the coating materials. CO<sub>2</sub> permeability of the coating materials increases in the order of multilayer textured coating material, emulsion paint, and thin textured coating materials.

Consequently, Eq. 6 can be suggested for evaluating the carbon dioxide permeation rate of a coating material.

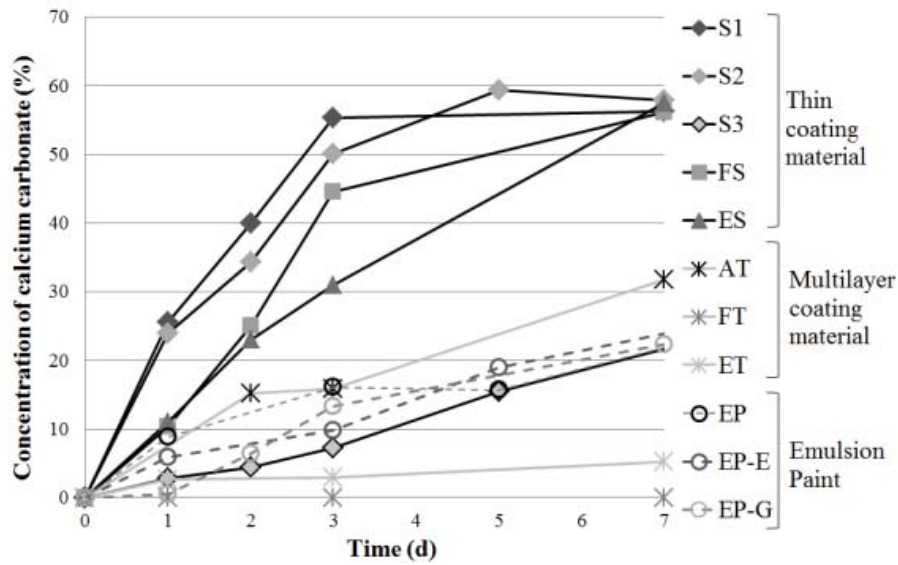


Figure 9.  $\text{CaCO}_3$  concentration in the laboratory dish over time (RH 59%,  $\text{Ca(OH)}_2$  Deposit 8g).

$$\alpha = (C_0 - C_t) \times M / (A \times t \times 100) \quad (6)$$

where  $\alpha$  is the carbon dioxide permeation rate of the coating material ( $\text{mol/m}^2 \cdot \text{d}$ ),  $A$  is the area of the specimens ( $\text{m}^2$ ),  $t$  is the testing time (day),  $M$  is the amount of deposit  $\text{Ca(OH)}_2$  (mol),  $C_{(0)}$  is the initial concentration of  $\text{Ca(OH)}_2$  (wt.%), and  $C_{(t)}$  is the concentration of  $\text{Ca(OH)}_2$  (wt.%) after the accelerated carbonation test.

## CONCLUDING REMARKS

The neutralization suppression performance of various types of finishing materials was evaluated using the neutralization depth determined from the amount of  $\text{CaCO}_3$  produced, instead of the phenolphthalein method. The integrated amount of  $\text{CaCO}_3$  produced in the mortar test specimens by the accelerated neutralization processing was measured, and the relationship between the integrated amount and the neutralization depth determined by the phenolphthalein method was investigated. The integrated amount of  $\text{CaCO}_3$  was found to be almost the same as the amount of  $\text{CaCO}_3$  estimated by assuming that all  $\text{Ca(OH)}_2$  in the neutralization region determined by the phenolphthalein method is changed to  $\text{CaCO}_3$  and that  $\text{Ca(OH)}_2$  in the un-neutralized region is not absolutely neutralized. Therefore, in this study, it was found that the  $\sqrt{t}$  law is also valid for the integrated amount of  $\text{CaCO}_3$ .

In addition to TGA analysis, the box method was developed in the study. This method enables rapid and simple evaluation of the carbon dioxide permeation rate.

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