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Carbonation degree of autoclaved aerated concrete

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Abstract

Neutralization depth has been the criterion in the carbonation or neutralization of ordinary concrete. On the other hand, autoclaved aerated concrete (AAC) has been investigated in terms of the carbonation degree. However, various definitions of carbonation degree of AAC have been proposed and applied. We have studied the definition of carbonation degree of AAC in order to investigate various research works under the same criterion. In this paper, we propose the carbonation degree (D_c) of AAC, D_c (%) = $(C-C_o)/(C_{max}-C_o)\times 100$ where C, C_o and C_{max} are the amount of carbon dioxide in the sample, in the non-carbonated sample and the theoretical amount of carbon dioxide needed to combine with the total calcium oxide in the sample to form calcium carbonate, respectively. In addition, we propose the heating weight loss from 600°C to 800°C in TG-DTA analyses as the method to determine the amount of carbon dioxide for carbonation degree of AAC. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbonation is one of the main factors of the aging deterioration of autoclaved aerated concrete (AAC), where tobermorite-11Å and well-crystallized C-S-H, the main structural minerals of AAC, react with carbon dioxide under the existence of moisture and finally decomposed to silica gels and calcium carbonate.

For the ordinary concrete, carbonation is the chemical reactions of low-crystallized C-S-H and calcium hydroxide with atmospheric carbon dioxide, leading to the neutralization that deprives concrete of the rust resistance for reinforcement steel bars. Therefore, the criterion of the neutralization depth has been favorably adopted. Many researchers have investigated their works by this criterion.

On the other hand, the main structural minerals of AAC are tobermorite-11Å and well-crystallized C-S-H, which are originally neutral because of the sufficient curing in an autoclave. Consequently, embedded reinforcement steel bars in AAC are coated with rust-resistant materials because AAC has no passivating effect on them. Carbonation of AAC leads to deterioration such as changes of minerals and microstructures, the degradation of properties, cracking and the increase of drying shrinkage. For these reasons, many studies have been made on carbonation of AAC and deterioration [1–7]. However, various definitions of carbonation degree of AAC have been proposed and applied making studies difficult to compare with each other. We have studied the definition of carbonation degree of AAC in order to investigate by a unified criterion in the same way as neutralization depth in concrete study.

2. Definition of carbonation degree of AAC

2.1. Carbonation of AAC

The raw materials of AAC, such as quartz sand, slag, cement and lime, are usually blended in a lower Ca/(Si + Al) ratio than 0.83, which is the theoretical Ca/(Si + Al) ratio of tobermorite-11Å. The foamed green body of AAC is cured sufficiently under the saturated vapor pressure at approximately 180°C in the autoclave. Accordingly, the main structural minerals of AAC are tobermorite-11Å and well-crystallized C-S-H,

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and almost all the calcium must exist in them. Tobermorite-11Å and well-crystallized C-S-H react chemically with carbon dioxide under the existence of moisture and are decomposed into silica gels and calcium carbonate as below,

$$5CaO \cdot 6SiO_2 \cdot 5H_2O \text{ (tobermorite} - 11\text{Å)} + 5CO_2 \\ \rightarrow 5CaCO_3 + 6SiO_2 + 5H_2O,$$

$$xCaO \cdot ySiO_2 \cdot zH_2O \text{ (well} - \text{crystallized C} - \text{S} - \text{H)} \\ + xCO_2 \\ \rightarrow xCaCO_3 + ySiO_2 + zH_2O.$$

The morphologies of tobermorite-11Å and well-crystallized C-S-H are platy. The morphology of silica gels decomposed from tobermorite-11Å and well-crystallized C-S-H are also platy, because calcium ions come out from them and combine with carbon dioxide to form calcium carbonate. Carbonation conditions, such as relative humidity, carbon dioxide concentration and curing time, affect the ratio of the polymorphs of calcium carbonate that form. [1] The content of tobermorite-11Å and well-crystallized C-S-H and the chemical compositions are not fixed because of the difference in composition of raw materials and the curing conditions in the autoclave by manufacturers. Consequently, carbonation degree must be applied for these various AAC in the same way.

2.2. Preceding research

Sauman [1] studied the relations between compressive strength and relative humidity, carbon dioxide concentration and curing time for accelerated carbonation. Sun et al. [2] proposed the ratio of compressive strength before and after carbonation as a criterion of carbonation. Compressive strength is, however, very strongly affected by bulk density and the shapes of samples.

Hanecka et al. [3] indicated the increase of bulk density as a criterion of carbonation. However, they could not describe the carbonation degree from the increase of bulk density because the amount of adsorbed water may have changed during carbonation.

Asano et al. [4] used the XRD peak intensities as a criterion for accelerated carbonation of laboratory-synthesized tobermorite-11Å. However, well-crystallized C-S-H can be hardly detected by XRD.

Dapkus and Stankevisius [5] and Iwasaki and Tada [6] proposed the carbonation degree as Eq. (1) at nearly the same time, where C, C_o and C_{max} are the amounts of carbon dioxide in the sample, in the non-carbonated sample and at the maximum carbonation, respectively.

$$(C - C_o)/(C_{max} - C_o) \times 100 \tag{1}$$

Dapkus and Stankevisius indicated an approximation of 2% for C_o and 16% for C_{max}. Iwasaki and Tada analyzed the amount of carbon dioxide by chemical analysis using hydrochloric acid, where C_o was that for non-carbonated AAC and C_{max} was that for fully carbonated AAC in accelerated conditions.

Sun et al. [2] and Ochiai [7] proposed the carbonation degree as Eq. (2) regardless of C_o in Eq. (1).

$$C/C_{max} \times 100 \tag{2}$$

Sun et al. analyzed the amount of carbon dioxide, C, by measuring the infrared absorption peak at 1430 cm^{-1} indicating calcium carbonate, where C_{max} was that for fully carbonated AAC in accelerated conditions. Ochiai analyzed the amount of carbon dioxide, C, by chemical analysis using hydrochloric acid and calculated C_{max} by the product of calcium oxide content, which was analyzed by XRF.

2.3. This study

As we mentioned above, almost all the calcium must exist in tobermorite-11Å and well-crystallized C-S-H. The maximum amount of carbon dioxide that combines with these calcium has not been evident, though Dapkus and Stankevisius [5] indicated an approximation of 16% for it and Iwasaki and Tada [6] analyzed it by chemical analysis using hydrochloric acid for fully carbonated AAC in accelerated conditions. In addition, chemical compositions of AAC made all over the world are different because of the variety of mix proportions. Consequently, it is precise and appropriate to define the carbonation degree of AAC by the molar ratio of calcium carbonate to the total amount of calcium oxide to compare with various research works. From a measurement point of view, it is better to be transformed to the weight/molar ratio of the amount of carbon dioxide in calcium carbonate to the amount of carbon dioxide where the total amount of calcium oxide combine with, in other words, theoretical maximum amount of carbon dioxide. However, in order to limit the changes during carbonation, the amount of carbon dioxide in non-carbonated samples must be subtracted.

Therefore, we propose the carbonation degree (D_c) of AAC (Eq. (3)),

$$D_c \text{ (\%)} = (C - C_o)/(C_{max} - C_o) \times 100 \tag{3}$$

where C, C_o and C_{max} are the amount of carbon dioxide in the sample, in the non-carbonated sample and the theoretical amount of carbon dioxide needed to combine with the total calcium oxide in the sample to form calcium carbonate, respectively. The total amount of calcium oxide has to be

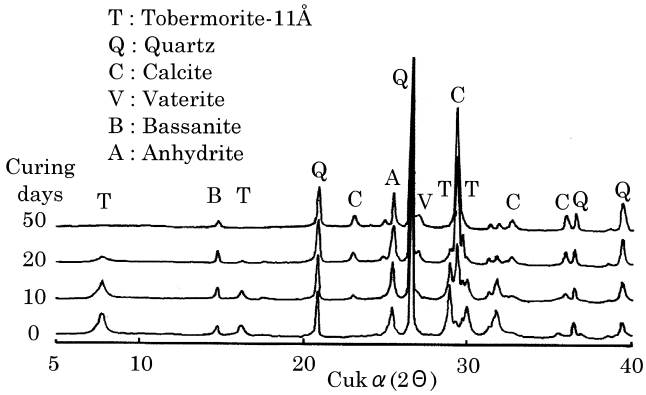

Fig. 1. XRD patterns for samples cured for 0, 10, 20 and 50 days.

analyzed by a reliable method such as ICP, while it is necessary to determine the measurement method of the amount of carbon dioxide.

3. Measurement method of carbonation degree of AAC

3.1. Samples

AAC blocks made by Sumitomo Metal Mining, Siporex Yokohama factory in Japan were used for analyses. They were shaped in 40 × 80 × 10 mm and subjected to carbonation process under the conditions of 20°C, 90% relative humidity and 3 vol.% carbon dioxide concentration for 0 (non-carbonated), 10, 20 and 50 days, respectively. Each sample was dried at 105°C for 2 h before analyses.

3.2. Experiment

There are several measurement methods to analyze the amount of carbon dioxide such as TG-DTA, IR spectrum during heating, chemical analysis using hydrochloric acid and so on. The analyzed values may be different from each other. We examined the first three methods to find suitable one.

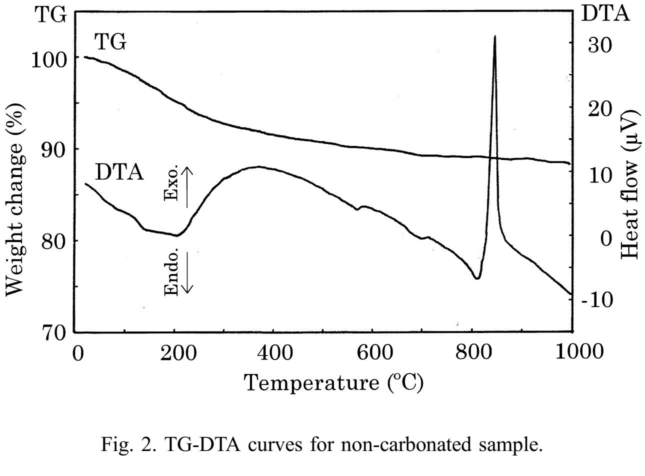

Fig. 2. TG-DTA curves for non-carbonated sample.

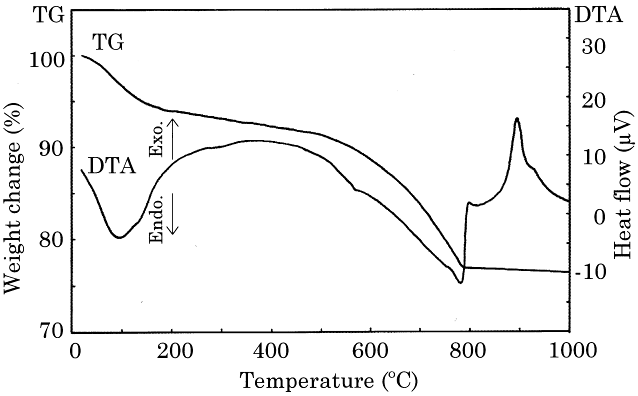

Fig. 3. TG-DTA curves for sample cured for 50 days.

‘TG-DTA’ was carried out under the conditions of nitrogen gas flow, rising temperature rate of 20°C/min and the temperature range from 20°C to 1000°C. ‘IR spectrum during heating’ was carried out as IR spectrum with quantitative analyses of carbon dioxide gas decomposed by heating at 1000°C. ‘Chemical analysis by hydrochloric acid’ was carried out by neutralizing of solutions containing carbon dioxide gas decomposed chemically by hydrochloric acid.

The amount of calcium oxide was analyzed by ICP. Crystal phases were characterized by XRD. Thermal decomposition of calcium carbonate in the 50-day carbonated sample, before and after calcining at 600°C and 800°C for 2 h was characterized by IR spectrum.

3.3. Results and discussion

XRD patterns are shown in Fig. 1. As the curing days increased, the changes of crystal phases due to carbonation were observed where calcium carbonate (calcite and

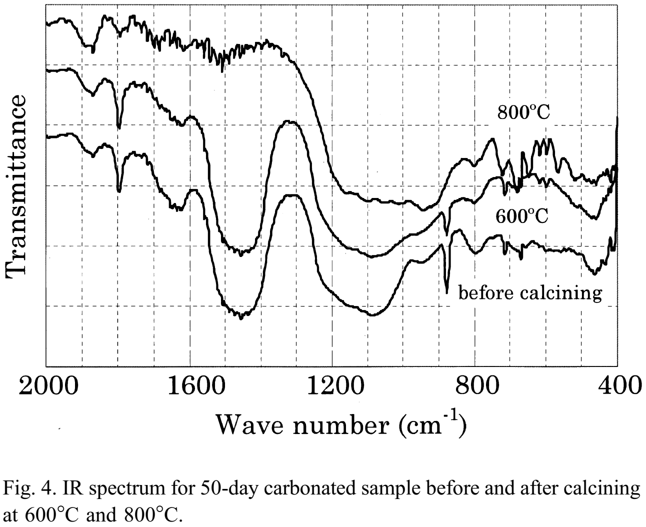

Fig. 4. IR spectrum for 50-day carbonated sample before and after calcining at 600°C and 800°C.

Table 1
The analyzed amount of carbon dioxide

	Amount of carbon dioxide (wt.%)		
Curing days	TG-DTA	IR spectrum during heating	Chemical analysis using hydrochloric acid
0 (non-carbonated)	0.91	2.64	1.78
10	4.93	7.70	6.98
20	9.38	12.5	12.0
50	11.8	15.8	15.9

vaterite) increased and tobermorite-11Å decreased and finally disappeared.

TG-DTA curves for the non-carbonated sample and the sample cured for 50 days are shown in Figs. 2 and 3, respectively. DTA curves show endothermic peaks at 700°C for the non-carbonated sample, 790°C for the sample cured for 50 days and 100–200°C and 570°C for each samples. The heat decomposition temperature of pure calcium carbonate crystal is 898°C and that of pure magnesium carbonate crystal, which is another possible carbonate salt in AAC decomposed at a temperature below 1000°C, is 540°C. IR spectrum for the 50-day carbonated sample before and after calcining at 600°C and 800°C for 2 h is shown in Fig. 4. IR peak at 1430 cm^{-1} indicating calcium carbonate [2] was observed before and after calcining at 600°C, however, it disappeared after calcining at 800°C. Accordingly, the endothermic peaks around 700–780°C in DTA curves may be attributed to the heat decomposition of calcium carbonate. Therefore, we can determine the amount of carbon dioxide in calcium carbonate as the heating weight loss from 600°C to 800°C to exclude magnesium carbonate and carbon dioxide adsorbed on the surface and dissolved in the adsorbed water.

The analyzed amounts of carbon dioxide by three methods are shown in Table 1. The amount of carbon dioxide determined by 'IR spectrum during heating' and 'chemical analysis' were bigger than that of 'TG-DTA' because the first two methods include all free carbon dioxide. The amount of carbon dioxide in magnesium carbonate may change during carbonation. Especially, the carbon dioxide adsorbed on the surface and dissolved in the adsorbed water may also change during carbonation because microstructure and specific surface area of carbonated AAC are changed [6]. Consequently, we propose the heating weight loss from 600°C to 800°C by TG-DTA analyses as the method to determine the amount of carbon dioxide for carbonation degree of AAC.

Table 2
Carbonation degree by TG-DTA and ICP

Curing days	Amount of carbon dioxide (wt.%) (TG-DTA)	Amount of calcium oxide (wt.%) (ICP)	Carbon degree (%)
0 (non-carbonated)	0.91	24.9	0.0
10	4.93	–	21.6
20	9.38	–	45.4
50	11.8	–	58.4

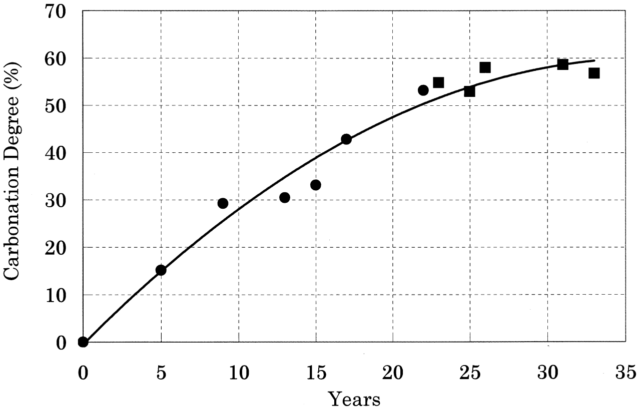

Fig. 5. Carbonation degree of in-service AAC panels.

Table 2 shows the carbonation degrees of the samples with TG-DTA for the amount of carbon dioxide and ICP for the amount of calcium oxide. With the method we proposed, it is possible to investigate carbonation of AAC more precisely than others.

4. Application of carbonation degree

The carbonation degrees of brand-new AAC panels and in-service AAC panels used for 5–33 years under nearly the same climate are shown in Fig. 5. The chemical compositions of them are shown in Table 3. The raw materials of AAC manufactured older than 23 years were quartz sand, cement and slag, while that younger than 23 years were quartz sand, cement and lime. Although the chemical compositions were different, the carbonation degree can be successfully applied. The

Table 3
The chemical compositions of brand-new and in-service AAC panels

	Chemical composition (wt.%)				
	ICP				TG-DTA
Years	CaO	SiO_2	Al_2O_3	Fe_2O_3	CO_2
0	24.9	49.8	2.57	1.66	0.91
5	26.7	51.4	2.64	1.42	3.95
9	24.9	52.7	2.51	1.46	6.36
13	28.8	47.0	2.76	1.52	7.53
15	29.7	46.6	2.41	1.68	8.34
17	24.8	50.7	2.21	1.28	8.86
22	27.9	45.3	3.22	1.57	12.08
23	27.4	32.6	8.75	0.76	12.21
25	24.2	36.0	10.20	2.05	10.49
26	25.7	38.0	9.34	1.67	12.09
31	25.4	37.9	7.07	1.71	12.07
33	24.9	39.3	9.36	1.56	11.50

carbonation degree that we proposed can work well for these various AAC.

5. Conclusions

We propose the carbonation degree (D_c) of AAC, D_c (%) = $(C-C_o)/(C_{max}-C_o)\times 100$ where C, C_o and C_{max} are the amount of carbon dioxide in the sample, in the non-carbonated sample and the theoretical amount of carbon dioxide needed to combine with the total calcium oxide in the sample to form calcium carbonate, respectively. In addition, we propose the heating weight loss from 600°C to 800°C in TG-DTA analyses as the method to determine the amount of carbon dioxide for carbonation degree of AAC. With the method that we proposed, it is possible to investigate carbonation of AAC more precisely than others.

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