MICROSTRUCTURE OF AUTOCLAVED AERATED CONCRETE
SUBJECTED TO CARBONATION
Durability of Autoclaved Aerated Concrete

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Abstract

Autoclaved Aerated Concrete (AAC) has been produced more than 30 years in Japan. Therefore, durability and service life of AAC become subjects of urgent study. Microstructure of AAC, which is related to cracking, changed during carbonation. Field AAC panels (Field-AAC) aged 5 to 33 years and laboratory-carbonated AAC blocks (Labo-AAC) were subjected to analysis. Microstructure of the samples was examined with XRD, TG-DTA, EPMA, mercury porosimeter, NMR, BET, and water vapour sorption isotherms and compared with the drying shrinkage data. Changes in peak of silicate structure in $^{29}$Si MAS NMR spectrum, approximately 1nm-micropore volume and drying shrinkage during carbonation were different between Field-AAC and Labo-AAC, while changes of crystalline phases (Tobermorite-11Å and calcium carbonate) and total pore volume were not different. It was concluded that the microstructure of silica-gels originated from the decomposed Tobermorite-11Å showed significant differences according to the carbonation conditions.

Keywords: AAC, microstructure, cracking, field sample, laboratory-carbonated sample, drying shrinkage, Tobermorite-11Å, calcium carbonate, durability, carbonation, $^{29}$Si MAS NMR, water vapour sorption isotherms,

1 Introduction

Autoclaved aerated concrete (AAC) has been produced in great quantity more than 30 years in Japan. Therefore, durability and service life of AAC become subjects of urgent study. One of the most effective factors for the durability of AAC is
carbonation in which Tobermörte-11Å (5CaO·6SiO$_2$·5H$_2$O), the main binding mineral of AAC, reacts with atmospheric carbon dioxide gas in the presence of moisture, and decomposed to silica-gel and calcium carbonate as eq. (1).

$$5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O} + 5\text{CO}_2 \rightarrow 5\text{CaCO}_3 + 6\text{SiO}_2 + 5\text{H}_2\text{O}$$ \hspace{1cm} (1)

Carbonation of the ordinary concrete, which is the reaction of CSH-gel and calcium hydroxide with carbon dioxide gas, leads to the loss of alkalinity and the rust resistance. That is why the neutralization is the major subject for carbonation of the ordinary concrete.

On the other hand, the main binding mineral of AAC is Tobermörte-11Å which is originally neutral because AAC is cured in the autoclave at 180°C and 10 atms sufficiently, regardless of several raw materials, such as quartz sand, cement, calcium oxide, slag and disposed AAC powders. The reinforced steel in AAC is coated with rust-resistant materials previously because Tobermörte-11Å doesn’t have an effect of that. Therefore, the subject for carbonation of AAC is not the neutralization but the changes of matrix itself. During carbonation, it is occurred that not only changes of minerals but also changes of microstructure which leads to the degradation such as decrease of strength and especially, growth of lattice-like cracking. That is why so many studies have been made for the changes of microstructure during carbonation.

(Sauman 1971, 1972) studied the changes of compressive strength, carbonation shrinkage and the ‘pseudomorphism’ shape-changes of Tobermörte-11Å crystals which showed that only the marginal parts of the crystals were somewhat frayed and unsharpened, under the accelerated conditions of 1-30 vol.% CO$_2$ and 50–100% R.H. (Sun et al. 1985) observed the 3 types of AAC samples made of different raw materials, by means of SEM after carbonation under the accelerated conditions of 50 vol.% CO$_2$ and 50 % R.H. They suggested that calcium carbonate deposited on the walls of air pores, silica-gel maintained the original network structure of Tobermörte-11Å, and these changes were not different among samples. (Iwasaki and Tada 1985) showed the changes of pore volume proportions with distinctions of submicro-, meso- and macro-pores by means of water vapour sorption isotherms and mercury porosimeter for the accelerated carbonated AAC under conditions of 20 vol.% CO$_2$ and 100 % R.H. (Ikeda et al. 1991) indicated that the silicate structures in Tobermörte-11Å were changed from double-chain structures to 3-dimensional framework structures by means of $^{29}$Si MAS NMR spectrum during carbonation under accelerated conditions of 10 vol.% CO$_2$ and 60 % R.H. However, these studies were all investigated for the accelerated carbonated AAC without correlating with the carbonation under practical conditions.

Several studies about the carbonation under practical conditions were investigated. (Hanecka et al. 1997) showed the increase of the specific gravity. (Dapkus and Stankevicius 1985) showed the increase of the amount of water content. However, the microstructure changes of AAC under practical conditions, which is extremely important to examine the durability and service life, have not been investigated yet. In addition, it is very important to make clear the difference of the microstructure changes between under practical conditions and accelerated conditions.
for prediction of degradation and remaining years by means of accelerated carbonation methods.

This study indicated the microstructure changes of AAC under practical conditions and accelerated carbonated conditions with reference to the approach of structural levels proposed by (Wittmann 1985).

2 Experimental

2.1 Samples

Field AAC panels (Field-AAC) aged 5 to 33 years under practical conditions, laboratory-carbonated AAC blocks (Labo-AAC) under accelerated conditions of 3 vol.% CO₂, 90% R.H. and 20°C, and non-treated AAC blocks (Nontreated-AAC) were subjected to analysis. Field-AAC were removed from several buildings in Japan. The usual climate in Japan is 0.03 vol.% CO₂, 25 to 95% R.H. and 0 to 35°C. Ordinary AAC blocks made by Siporex Yokohama factory of Sumitomo Metal Mining Co., Ltd were used for Labo-AAC and Nontreated-AAC. They were shaped in 80*40*10mm for several analysis and 40*40*160mm for measuring length changes.

2.2 Measurement of the degree of carbonation

The amount of combined carbon dioxide and calcium oxide were measured to determine the degree of carbonation. TG-DTA was used for analysis of the amount of combined carbon dioxide excluding the amount of adsorbed carbon dioxide gas and carbonated salt other than calcium carbonate. The amount of combined carbon dioxide were measured as the weight loss from 600 to 800°C corresponding to the decomposition of calcium carbonate. The amount of calcium oxide was analysed by ICP. The degree of carbonation (Dc) can be given by

\[ Dc (%) = \frac{\left( \frac{C - C_0}{C_{\text{max}} - C_0} \right) \times 100}{1} \]

where C, C₀ and C₀ are the amount of combined carbon dioxide for each samples, that of Nontreated-AAC and that when all calcium oxide become calcium carbonate.

2.3 Analysis of crystalline phases and microstructure

Crystalline phases were analysed by XRD. Microstructure was analysed by mercury porosimeter, EPMA, SEM, BET specific surface area analyzer, water vapour sorption isotherms and ²⁹Si MAS NMR.

2.4 Measurement of drying shrinkage

Drying shrinkage was measured as the length change from the saturated water condition to the equilibrium state under 45% R.H.

3 Results and discussion

3.1 Degree of carbonation (Dc)

Changes of Dc for Field-AAC and Labo-AAC as a function of time are shown
in Fig.1(a) and (b), respectively. For Field-AAC, Dc increased with exposed years and saturated to 60% approximately after 30 years. For labo-AAC, Dc increased with treated days and saturated to 60% approximately after 40 days. In the following discussion, Dc will be used as the basis for estimation because the changes of Dc were very similar between Field-AAC and Labo-AAC.

![Fig.1: Dc for (a) Field-AAC and (b) Labo-AAC](image)

3.2 Changes of crystalline phases

Changes of crystalline phases of Field-AAC and Labo-AAC analysed by XRD are shown in Fig.2(a) and (b), respectively. In both samples, changes of crystalline phases are similar. With increase of Dc, Tobermorite-11Å decreased and calcite increased. When Dc was 30%, vaterite began to increase. Therefore, the decomposition of Tobermorite-11Å and the deposition of calcium carbonate were similar to each other though carbonation rate was different extremely because of the differences of atmospheric carbon dioxide concentration and relative humidity.

![Fig.2: XRD peak intensity for (a) Field-AAC and (b) Labo-AAC](image)
3.3 Changes of microstructures in levels of 10nm to µm

Pore size distributions by mercury porosimeter of Nontreated-AAC, Field-AAC (Dc=60%) and Labo-AAC (Dc=60%) are shown in Fig.3. The total pore volume of Field-AAC and Labo-AAC decreased from 0.8ml/g to 0.6ml/g by carbonation, particularly in the typical pores of AAC around 10 to 1000nm corresponding to interparticle pores of Tobermorite-11Å (Prim and Wittmann 1983).

Ca and Si distributions for Nontreated-AAC, Field-AAC (Dc=60%) and Labo-AAC (Dc=60%) by EPMA cross-section analysis are shown in Fig.4. For both Field-AAC and Labo-AAC, the distribution of Ca atoms deposited locally in the matrix during carbonation, though the distribution of Si atoms unchanged. It was observed that Ca ions migrated from Tobermorite-11Å and reacted with carbon dioxide gas, though Si ions remained.

Fig.3: Pore size distribution by mercury porosimeter
SEM micrographs in air pores for Nontreated-AAC, Field-AAC (Dc=60%) and Labo-AAC (Dc=60%) are shown in Fig.5. The shapes of Tobermorite-11Å particles for Nontreated-AAC were planer. For carbonated samples, the shapes of silica-gels, which is called silica-skeleton, originated from decomposed Tobermorite-11Å were different slightly. For Labo-AAC, only the marginal parts of the silica-gels were somewhat frayed and unsharpened as shown in the preceding studies (Sauman 1972). On the other hand for Field-AAC, the shapes of silica-gels were similar to those of Tobermorite-11Å of Nontreated-AAC. Anyway, the planer particle shapes and the interparticle pores by geometrical arrangement of those were not changed significantly during carbonation under both practical and accelerated conditions. Therefore, it was clear that the decrease of pore volume during carbonation was caused by the deposition of calcium carbonate into the interparticle pores around 10 to 1000nm.
3.4 Changes of microstructures in levels of atomic arrangement to 10nm

The changes of BET specific surface area are shown in Fig.6. For Labo-AAC BET specific surface area increased from 20 to 60 m$^2$/g during carbonation. For Field-AAC, however, it was decreased to 10 m$^2$/g. The pore size distribution by BET specific surface area is shown in Fig.7. Micropores approximately 1 and 6 nm can be observed for Nontreated-AAC. All ranges of micropores decreased for Field-AAC. Micropore volume of approximately 1 nm increased extremely for Labo-AAC. It was observed that these differences of pore structures around nanometer levels, which had great influence to BET specific surface area, indicated the differences of structures in silica-gels between Field-AAC and Labo-AAC because crystallines of calcium carbonate were large enough to be detected by XRD.

Water vapour sorption isotherms for Nontreated-AAC, Field-AAC (Dc = 60%) and Labo-AAC (Dc = 60%) are shown in Fig.8. It was recognised that there was hysteresis loop only for Field-AAC. This was type B hysteresis loop classified by de Boer indicating pore structures of slit or parallel plane. It was observed that silica-gels of Field-AAC had layered structures in which adsorption and desorption of water were possible. Spectrum of $^{29}$Si MAS NMR for Nontreated-AAC, Field-AAC (Dc = 60%) and Labo-AAC (Dc = 60%) are shown in Fig.9. Chemical shifts of $^{29}$Si MAS NMR are shown in Table 1. For Nontreated-AAC, $Q^2$ and $Q^3$ spectrum which indicated the silicate double-chain structures were found as reported by (Wieker et al. 1982). For Labo-AAC, $Q^4$ spectrum which indicated the silicate 3-dimentional framework structures similar to ordinary silica-gels were found as reported by (Ikeda et al. 1991). For Field-AAC, however, $Q^3$ spectrum, which indicated the silicate sheet-like structures and had not been reported yet, were found.
Fig. 8: Water vapour sorption isotherms

Tobermorite-11Å has layered structures in which silicate double-chain structures are sandwiched between CaO layers. For Field-AAC, carbonation reaction was relatively slow and mild because carbon dioxide gas concentration was as low as 0.03 vol.% in the air. Therefore, it was observed that the silicate structures were rearranged slightly from double-chain to sheet-like structures and the crystalline became bigger just like Ostwald ripening during carbonation under practical condition. It was also observed for Field-AAC that the layered structures of silica-gel was the result of the silicate sheet-like structures and the planer particle shapes of Tobermorite-11Å were not changed because of the moderate rearrangement of silicate structures.

Fig. 9: $^{29}$Si MAS NMR spectrum for (a) Nontreated-AAC, (b) Fields-AAC (Dc=60%) and (c) Labo-AAC (Dc=60%)
For Labo-AAC, on the other hand, ambient carbon dioxide gas concentration was as high as 3 vol.% in the atmosphere, so that carbonation reaction was very rapid and hard. Therefore, it was observed for Labo-AAC that the silicate structures were rearranged extremely from double-chain to 3-dimensional framework structures and the crystalline were divided smaller resulting in the increases of BET specific surface area and approximately 1 nm-micropore volume. It was also observed for Labo-AAC that the marginal parts of planer particle shapes of Tobermorite-11Å were altered to somewhat frayed and unsharpened because of the considerable rearrangement of silicate structures.

Table 1: Chemical shifts of $^{29}$Si MAS NMR

<table>
<thead>
<tr>
<th>ppm from TMS</th>
<th>$Q^2$</th>
<th>$Q^3$</th>
<th>$Q^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1Al</td>
<td>0Al</td>
<td>1Al</td>
</tr>
<tr>
<td>Non-treated AAC</td>
<td>-80.3</td>
<td>-85.1</td>
<td>-91.9</td>
</tr>
<tr>
<td>Field-AAC (Dc=60%)</td>
<td>-87.3</td>
<td>-99.3</td>
<td></td>
</tr>
<tr>
<td>Labo-AAC (Dc=60%)</td>
<td></td>
<td></td>
<td>-103</td>
</tr>
</tbody>
</table>

( ) ; Relative peak intensity * ; Quartz

3.5 Drying shrinkage

Drying shrinkage as a function of Dc is shown in Fig.10. Drying shrinkage increased with the increase of Dc from 0.03% to 0.06% and 0.11% for Field-AAC and Labo-AAC, respectively. Drying shrinkage of AAC is the result of that of Tobermorite-11Å or silica-gels which are the main binding minerals for Non-treated and carbonated AAC. Therefore, it was observed that the increase of drying shrinkage was mainly due to the change of main binding minerals from Tobermorite-11Å to silica-gels. It was also observed that changes of silica-gel structure in Labo-AAC were more excessive than that in Field-AAC so that drying shrinkage for Labo-AAC was larger than that for Field-AAC. In other words, behaviour of macro-level such as drying shrinkage was influenced by microstructure such as atomic arrangement or crystalline structures.
Fig. 10: Drying shrinkage as a function of $D_c$

4 Conclusions

Microstructure changes of AAC were investigated during carbonation under practical conditions, Field-AAC and accelerated conditions, Labo-AAC.

Changes of crystalline phases and microstructures of 10nm to µm were similar between Labo-AAC and Field-AAC as follows;
(1) $D_c$ increased with time and saturated at 60%.
(2) With increase of $D_c$, Tobermorite-11Å decreased and calcite increased. After $D_c$ reached 30%, vaterite increased.
(3) The pore volume decreased and the Ca atoms were deposited locally in the matrix.
(4) The planer particle shape and the interparticle pores were not changed significantly.

Changes of microstructures of atomic arrangement to 10nm and drying shrinkage were different between Labo-AAC and Field-AAC as follows;
(5) BET specific surface area increased from 20 to 60 m$^2$/g for Labo-AAC, but decreased to 10 m$^2$/g for Field-AAC. Micropore volume of approximately 1 nm increased extremely for Labo-AAC.
(6) Hysteresis loop indicating the layered structures on the water vapour sorption isotherms were observed only in Field-AAC.
(7) In the $^{29}$Si MAS NMR spectrum, $Q^4$ spectrum indicating the silicate 3-dimentional framework structures were found for Labo-AAC, however, $Q^3$ spectrum indicating the silicate sheet-like structures were found for Field-AAC.
(8) Drying shrinkage increased with increase of $D_c$ from 0.03% to 0.06% and 0.11% for Field-AAC and Labo-AAC, respectively.
5  Acknowledgments

The authors are grateful to Prof. K. Okada and Mr. Y. Kameshima of Tokyo Institute of Technology, for their support in the measurement of water vapour sorption isotherms.

6  References


