Scientific paper

Phase Assemblage, Microstructure and Shrinkage of Cement Paste during Carbonation at Different Relative Humidities

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Abstract

This study investigates the effect of relative humidity (RH) on the carbonation of hydration products. The samples of ordinary Portland cement (OPC) and OPC/blast furnace slag paste were exposed to accelerated carbonation under 3% CO₂ concentration at different RHs from 11% to 85%. Thermogravimetric/differential thermal analysis and X-ray diffraction/Rietveld analysis were performed to quantify the amount of portlandite and calcium carbonate polymorphs. The Ca/Si ratio of the carbonated C-S-H phase was determined using a phase equilibrium calculation. To evaluate the microstructural changes in carbonated samples, water vapor sorption and nitrogen sorption measurements were conducted before and after carbonation. Results show that the carbonation shrinkage progressively increased at intermediate RHs (43% and 66% RH). The relation between carbonation shrinkage and the Ca/Si ratio of C-S-H agrees with the change of C-S-H mean chain length. There were significant changes in the carbonation rates of C-S-H and portlandite at different RHs. The coarsening of the meso scale pore likely derives from the polymerization and aggregation of C-S-H due to decalcification. This paper is an extended and enhanced version of an earlier study (Suda, Y., Tomiyama, J., Saito, T. and Saeki, T., 2020). “Impact of relative humidity on carbonation shrinkage and microstructure of hardened cement paste.” In: Proc. 6th International Conference on Construction Materials (ConMat’20), Fukuoka, Japan 27-29 August 2020. Tokyo: Japan Concrete Institute.

1. Introduction

Carbonation of concrete leads to the corrosion of steel bar in a reinforced concrete structure. It is important to assess the carbonation behavior of reinforced concrete structures because of their long-term service. Carbonation kinetics is influenced by various conditions such as concrete materials, mineral admixture, temperature, relative humidity (RH), inside or outside, and CO₂ concentration. The carbonation process on concrete involves the diffusion of CO₂, the dissolution of calcium bearing hydration products such as portlandite and calcium silicate hydrate (C-S-H), and the precipitation of calcium carbonate in pore space. Hence, the presence of water as a reaction medium is essential for carbonation reaction in concrete. Since the moisture condition in concrete is influenced by RH, it has been found that carbonation progress is faster at intermediate humidity (50 to 70%) (Verbeek 1958; Parrot 1991; Galen 2013).

In the case of carbonation on hydration products, previous studies have shown that the carbonation progress of calcium hydroxide nanoparticles at higher RH is faster than that at lower RH (López-Arce et al. 2011). For the carbonated cement paste with CEM I and CEM V/A (Drouet al. et al. 2019), at higher RH, calcite was formed as mainly calcium carbonate, while the aragonite, and vaterite of calcium carbonate polymorphs was observed at lower RH. In addition, the maximum carbonation depths of hardened cement pastes were seen around 50% RH. Meanwhile, the carbonation rates on the powder samples obtained by synthesized hydration products, which are portlandite, C-S-H with different Ca/Si ratios and ettringite, increase with increasing RH (carbonation rates at 90% RH are greater than at 57% RH) (Steiner et al. 2020). The results for the carbonation rates of powder sample differ from the real carbonation rate of hardened sample showing maximum at intermediate RH. Since the hardened cement pastes are a microporous material, water is retained in the pore space. On the other hand, the particle samples might be difficult to form a water film on the surface for carbonation process (dissolution and precipitation) (Galan et al. 2015). Hence, it seems that the water content is not the same for hardened cement paste samples and stack of particles for a common RH. Thus, the effect of RH on hydration products in hardened cement paste remains to be investigated.

Moreover, the carbonated specimens rearrange the pore structure such as the alternation of pore size distribution and pore volume (Pihlajaavaara 1968; Ngala and Page 1997; Morandeau et al. 2015; Wu and Ye 2017). Recent studies showed that the carbonation shrinkage leads to the micro-crack for specimens, including a high
amount of fly ash, blast furnace slag and silica fume (Borges et al. 2010; Auroy et al. 2015; Dutzer et al. 2019). This microstructural change and/or the development of micro-crack increase the diffusivity of gas and water vapor for carbonated specimens containing the fly ash and blast furnace slag (Leemann et al. 2017; Auroy et al. 2015; Dutzer et al. 2019; Boumaaza et al. 2020). The generation of the microstructural change and micro-crack could be explained by the shrinkage induced by the C-S-H de-calcification involving the polymerization of silicate anion due to carbonation (Chen et al. 2006). Although the qualitative discussion is mentioned, the relation between microstructural change and the carbonation shrinkage has not been sufficiently shown in the quantitative evaluation of the C-S-H decalcification process.

There have been limited studies on the impact of RH and binder types on carbonation shrinkage and phase assemblage. Thus, this study’s objective is to conduct the quantitative estimation for the effect of RH on the carbonation kinetics of hardened cement paste with and without blast furnace slag (BFS). The effects of the carbonation kinetics of hardened cement paste with and without blast furnace slag (BFS) were chosen to investigate the samples with various binder types of each material are listed in Table 1. The specimens were prepared as cement paste. The water-to-binder ratio was fixed at 0.55 for the OPC, and OPC/BFS pastes. The physical properties and chemical compositions of each material are listed in Table 1.

| OPC | BFS |
|-----|-----|
| Density (g/cm³) | 3.16 | 2.91 |
| Blaine (cm²/g) | 3420 | 4180 |
| Ig. loss (%) | 0.64 | 0.09 |

2. Experimental procedure

2.1 Materials and sample preparation

Ordinary Portland cement (OPC) and BFS were used as cementitious materials. OPC was replaced by 50% BFS. The specimens were prepared as cement paste. The water-to-binder ratio was fixed at 0.55 for the OPC, and OPC/BFS pastes. The physical properties and chemical compositions of each material are listed in Table 1.

Each paste was mixed for 3 minutes and then mixed regularly to prevent bleeding. After being mixed, each fresh cement paste sample was placed into molds (20×80×4 mm) and vibrated to remove entrapped air. The paste in the molds was cured for 24 h in a sealed condition at 20°C and then demolded. The hardened cement paste samples were immersed in a saturated Ca(OH)₂ solution to prevent calcium leaching. The initial curing of the cement paste lasted 28 days.

2.2 Accelerated carbonation test

After the 28-day initial curing period, the paste samples were removed from the saturated Ca(OH)₂ solution, and their surfaces were polished by using a scraper. Before accelerated carbonation, these samples were placed in a desiccator at 20°C and different RHs (11%, 43%, 66% and 85%) for about five months. Each of these were controlled by using a specific saturated salt solution. LiCl (11% RH), Zn(NO₃)₂·6H₂O (43% RH), CoCl₂·6H₂O (66% RH), and KCl (85% RH) were used as saturated salts solutions (Greenspan 1977). A NaOH solution was also added to the desiccator as a carbon dioxide absorbent. The RHs were monitored with a temperature and humidity sensor that has a measuring precision of ±3.0%.

Accelerated carbonation was achieved under the aforementioned temperature and humidity conditions at pre-drying. The pre-dried samples were exposed to a CO₂ environment in a desiccator without a NaOH solution for 1, 3, 7, 14, 28, 56 and 91 days. These carbonation times were chosen to investigate the samples with various degree of carbonation. The CO₂ concentration in the gas used for accelerated carbonation was 3% (97% nitrogen and 3% carbon dioxide). This CO₂ concentration was selected to represent the carbonation process of hydration products (mainly C-S-H) and microstructural change similar to natural carbonation (Castellote et al. 2009; Auroy et al. 2018). The mixed gas was added into a desiccator at a flow rate of 200 ml/min for 4 h/day, and the desiccator was sealed by closing the stopcock annexed to it.

2.3 Test methods

2.3.1 Length change measurements

The length change of the samples after drying and carbonation at different RHs was measured by a displacement transducer with a measurement precision of 0.0001 mm. The shrinkage strain was determined from the difference between each sample and a reference (using Invar). The carbonation shrinkage strain was calculated by subtracting the drying shrinkage strain from the total shrinkage strain (sum of drying and carbonation shrinkages) at different RHs. Four or five replicates were tested for the length change measurement. The average value for each replicate was adapted as test results.

2.3.2 Thermogravimetric analysis

For sample preparation, the cement paste samples were crushed into particles smaller than 90 μm. The samples were then oven-dried at 110°C under vacuum for three hours. Thermogravimetric (TG)/differential thermal analysis (DTA) was conducted using a Rigaku Thermo
Plus EVO2 thermodilatometer. The dried samples were heated at 10°C/min from 30 to 1000°C under nitrogen flow in the TG/DTA instrument. The ignition loss in the samples was calculated from their weight reduction upon heating from 30 to 1000°C. To prevent the mass increase due to sulfide oxidation in the BFS, the hydrated samples containing BFS was calculated from their weight reduction upon heating from 30 to 900°C. The amount of calcium hydroxide was calculated by the weight loss from the peak area of the DTG around 450°C. The amount of calcium carbonate in each sample was determined from the weight loss at 550 to 800°C.

The consumption ratio of calcium hydroxide from acceleration carbonation was determined from Eq. (1).

\[
CH_{CR,t} = \frac{[CH]_{n\%RH_{dry}} - [CH]_{n\%RH_{carb,t}}}{[CH]_{n\%RH_{dry}}} \times 100
\]  

where \( CH_{CR} \) is the consumption ratio of calcium hydroxide from acceleration carbonation at each carbonation period, \([CH]_{n\%RH_{dry}}\) is the amount of calcium hydroxide in the non-carbonated dry sample at different RHCs (n=11% 43%, 66% and 85%) for five months and \([CH]_{n\%RH_{carb,t}}\), the amount of calcium hydroxide in the carbonated sample on each time at the four different RHCs mentioned above.

### 2.3.3 X-ray diffraction/Rietveld analysis

The cinder and hydration product contents were measured by the X-ray diffraction (XRD)/Rietveld method. After the initial curing and 91 days of carbonation time, the cement paste samples were broken into small pieces, and these small pieces were ground and sieved through a 90 μm mesh. The powder samples were immersed in acetone under vacuum for three hours, and the solid and aqueous phases were then separated by filtration. The solid phase was dried at 11% (using a saturated LiCl aqueous solution) over 14 days. The mineralogical compositions induced by carbonation were determined by the X-ray diffraction (XRD)/Rietveld method. The thermodynamic phase equilibrium calculation was conducted by PHREEQC Version 3 of geochemical code using the CEMDATA18.1 database (Lothenbach et al. 2019). Hydrogarnet phase was used as the solid solution of Ca₅Si₅O₁₄·H₂O and Ca₃Al₄O₁₀·H₂O for the C-S-H phase, the Ca/Si ratio in the OPC paste sample is higher than that in the OPC/BFS paste sample (Taylor et al. 2010). To consider the difference of Ca/Si ratio of C-S-H phase in OPC and OPC/BFS on the thermodynamic phase equilibrium calculation, the CSHQ model was used for OPC paste samples, and the CSH3T model was used for OPC/BFS paste samples. The range of Ca/Si ratio is 0.67 to 1.63 for CSHQ model and 0.67 to 1.50 for CSH3T model.

### 2.3.4 Phase equilibrium analysis

The thermodynamic phase equilibrium calculation determined the phase assemblage of carbonated cement paste samples. The thermodynamic phase equilibrium calculation was conducted by PHREEQC Version 3 of geochemical code using the CEMDATA18.1 database (Lothenbach et al. 2019). Hydrogarnet phase was used as the solid solution of Ca₅Si₅O₁₄·H₂O and Ca₃Al₄O₁₀·H₂O for the C-S-H phase, the Ca/Si ratio in the OPC paste sample is higher than that in the OPC/BFS paste sample (Taylor et al. 2010). To consider the difference of Ca/Si ratio of C-S-H phase in OPC and OPC/BFS on the thermodynamic phase equilibrium calculation, the CSHQ model was used for OPC paste samples, and the CSH3T model was used for OPC/BFS paste samples. The range of Ca/Si ratio is 0.67 to 1.63 for CSHQ model and 0.67 to 1.50 for CSH3T model.

The phase assemblage of non-carbonated cement paste was calculated from the reaction ratio of each cinder minerals and BFS (OPC/BFS paste) after initial curing (at 28 days) and the minor chemical composition (MgO, SO₃, Na₂O, and K₂O), as shown in Table 1. The reaction ratio of cinder minerals was determined by XRD/Internal standard method using the integrated intensity of cinder minerals, which was calculated using the peak deconvolution by pattern fitting (Igarashi et al. 2011). The phase assemblage of carbonated cement paste was determined by the reaction analysis between the initial hydration products (non-carbonated) and CO₂. The results of TG/DTA were used as the reacted CO₂ on the thermodynamic phase equilibrium calculation.
2.3.5 Nitrogen sorption test
A MicrotracBEL BELSORP-mini II measured the nitrogen adsorption isotherms of the samples. The carbonated cement paste samples on 0 day and 91 days at different RHs were crushed into particles sized 2.5 to 5.0 mm, then dried via vacuum de-aeration at 110°C for 1 h. The nitrogen adsorption isotherm test was conducted at $-196°C$. The specific surface area of each sample was determined by the Brunauer-Emmett-Teller (BET) method.

2.3.6 Water vapor sorption test
The water vapor isotherms of adsorption and desorption scanning curve were conducted by the gravimetric method using saturated salt solutions. The carbonated cement paste samples on 0 day and 91 days at different RHs were measured. The water vapor sorption experiments were started from an adsorption process. All samples were crushed into particles sized 2.5 to 5.0 mm, dried on vacuum de-aeration at 110°C for 12 h. In this study, this drying condition at 110°C was defined as 0% RH. The dried samples were set into a desiccator with a specific saturated salt solution, as shown in Table 2. The desiccators were placed in the constant temperature room conditioned at 20°C. The samples, shown in an adsorption equilibrium state at 97% RH, were shifted to a desorption scanning process at different RHs. The specific surface area of each sample was calculated by the BET method using the adsorbed water at 11%, 22% and 33% RH.

The degree of water saturation was calculated from the mass difference between saturated and dried state at 110°C.

3. Results
3.1 Change in shrinkage strain by carbonation
Figures 1(a) and 1(b) show the total shrinkage strain (sum of drying and carbonation shrinkages) changes during carbonation at different RHs for the OPC, and OPC/BFS pastes. The total shrinkage strains at 0 days express the drying shrinkage. The total shrinkage strains at different RHs increased with the period of carbonation. Samples at 43% and 66% RH showed rapid progress of the total shrinkage strain, whereas the progress at 11% and 85% RH was slow for both the OPC and OPC/BFS pastes. The tendency of the total shrinkage strain to increase at intermediate humidity was according to a previous result (Verbeck 1958; Kamimura et al. 1965). The total shrinkage strain of the OPC/BFS paste was lower than that of the OPC paste at 43% and 66% RH. Figures 2(a) and 2(b) show the evolutions in the carbonation shrinkage strain over time at different RHs for the OPC and OPC/BFS pastes. The carbonation shrinkage of samples at 43% and 66% RH progressively increased.

3.2 Reduction of calcium hydroxide and formation of calcium carbonate
Figure 3 shows the reduction of calcium hydroxide by carbonation. The calcium hydroxide of the carbonated OPC paste at 66% RH started to reduce from 3 days. The calcium hydroxide on 91 days was almost consumed. Samples at 43% RH showed a rapid reduction of the calcium hydroxide on 28 days, while the decrease at 85% RH was slow. The amount of calcium hydroxide of OPC/BFS paste shows a similar tendency. At 43% and 66% RH, the amount of calcium carbonate of the OPC paste increased from 3 days of carbonation (Fig. 4). The calcium carbonate contents of carbonated OPC/BFS paste were less than that of OPC paste. These results were determined from the mass difference between saturated and dried state at 110°C.

Table 2 List of saturation salt solutions used on adsorption and desorption scanning curve.

| Saturated salt solution | RH   |
|-------------------------|------|
| LiCl                    | 11%  |
| CH₃COOK                 | 22%  |
| MgCl₂·6H₂O              | 33%  |
| K₂CO₃                   | 43%  |
| Mg(NO₃)₂·6H₂O           | 56%  |
| NaNO₃                   | 66%  |
| NaCl                    | 75%  |
| KCl                     | 85%  |
| Mg(NO₃)₂·6H₂O           | 90%  |
| KNO₃                    | 93%  |
| K₂SO₄                   | 97%  |

\[
S_w = \frac{\text{Abs}_{\text{abs} \text{RH}}}{\text{Abs}_{\text{sat}}} \times 100
\]
reflect amount of calcium oxide in binder of OPC (CaO: 65.2%) and OPC/BFS (CaO: 53.9%).

### 3.3 Relation between calcium carbonate and carbonation shrinkage strain

Figure 5 shows the relation between the calcium carbonate content and carbonation shrinkage strain at 43%, 66% and 85% RH. In this figure, the filled and open symbols denote OPC paste and OPC/BFS paste, respectively. At 43% RH, the carbonation shrinkage strain increased with increasing the calcium carbonate content. Meanwhile, at 66% RH, when the calcium carbonate content exceeded about 30% for the OPC paste and about 17% for the OPC/BFS paste, the carbonation shrinkage strain increased rapidly. Additionally, the relation between the carbonation shrinkage strain and calcium carbonate of the OPC/BFS paste was larger than that of the OPC paste at the common RH.

### 3.4 Relation between calcium carbonate and consumption ratio of calcium hydroxide

The relation between calcium carbonate content and consumption ratio of calcium hydroxide is estimated to investigate the effect of carbonation on calcium hydroxide and C-S-H. The relation of both is shown in Figs. 6(a) and 6(b). For OPC paste, the calcium carbonate and the consumption ratio of calcium hydroxide increased with RHs. For OPC/BFS paste sample, the slopes of the sample at 66% and 85% RH are shown to be higher than that at 43% RH. These results reflect that the carbonation behavior of portlandite and C-S-H differs depending on RHs. Recent studies show that the synthesized portlandite and the portlandite in synthesized C-S-H with a Ca/Si ratio of 1.50 remain completely unconsumed due to carbonation at the intermediate RH (54% and 57% RH, respectively) (López-Arce et al. 2011; Steiner et al. 2020).
3.5 Quantitative evaluation of calcium carbonate polymorphs and an amorphous phase by equilibrium analysis

3.5.1 XRD patterns
The XRD patterns of the carbonated OPC and OPC/BFS paste for 91 days are shown in Figs. 7(a) and (b). These XRD charts show the peak of calcite (c), aragonite (A), vaterite (V), portlandite (P), monosulphate (MS), ettringite (Ett), and $\alpha$-Al_{2}O_{3} (I). Calcite was formed in the OPC and OPC/BFS paste at all RHs. Vaterite was produced at 43%, 66% and 85% RH. The OPC paste at 43% RH observed aragonite formation. No monosulphate peak was detected for the sample at 66% RH. Hence, all the monosulphate of the sample at 66% RH decomposed because of carbonation. Besides, given that the calcium carbonate contents of the sample at 43% and 66% RH were almost the same, as shown in Fig. 4, the carbonation at low RH (under 43% in this study) seemed to restrain the monosulphate decomposition.

3.5.2 Rietveld analysis
The quantitative estimation of calcite, aragonite, and vaterite among the calcium carbonate polymorphs was conducted by Rietveld analysis. The decomposition of the C-S-H phase was estimated using Eq. (3). The amorphous phase calculated by Eq. (2) for the OPC/BFS was also included in the non-reacted glass phase in BFS. Assuming that the reaction of glass phase in the BFS did not proceed during carbonation, the amount of C-S-H of OPC/BFS was obtained by subtracting the non-reacted glass phase content from the amorphous phase calculated by Eq. (2).

The total amounts of calcium carbonate and the decomposition ratio of C-S-H for the OPC and OPC/BFS paste on 91 days of carbonation are shown in Figs. 8(a) and 8(b). OPC paste at 66% and 85% RH formed calcite as the main calcium carbonate polymorphs, while sample at 43% RH formed vaterite and a small amount of aragonite. For the OPC/BFS paste, the main calcium carbonate polymorphs at 43%, 66% and 85% RH were:

- 11% RH
- 43% RH
- 66% RH
- 85% RH

Fig. 7 XRD patterns of carbonated samples on 91 days for (a) OPC and (b) OPC/BFS.
vaterite. Previous studies have investigated such calcium carbonate polymorphs by Raman spectrometry for synthesized C-S-H with different Ca/Si ratios exposure to the atmosphere (Black et al. 2007). As a result, the formation of calcite has not been detected for all synthesized C-S-H, while vaterite has been produced because of the carbonation of C-S-H. Besides, the transformation from vaterite to stable calcite is restricted when the carbonation condition is the low RH or the adsorbed water is a small amount (Maruyama et al. 2018; Steiner et al. 2020).

From Fig. 8, it can be seen that a significant decrease in C-S-H due to carbonation was observed for the OPC and OPC/BFS paste at 43% RH. The carbonation tendency of C-S-H was according to the formation of vaterite at the different RHs. The decomposition ratio of C-S-H for the OPC/BFS paste was equal to that of the OPC paste at different RHs, despite the small amount of calcium carbonate phase.

Therefore, given that the carbonation of C-S-H forms vaterite and aragonite, the carbonation of C-S-H appeared to progress at 43% RH in comparison with that at 66% RH. In the case of the OPC pastes at 66% and 85% RH, the formation of calcite as the main calcium carbonate seemed to promote the carbonation of portlandite. A comparison of the OPC and OPC/BFS pastes revealed that vaterite was the main calcium carbonate mineral for the OPC/BFS paste at 43, 66 and 85% RH. To form the vaterite at 66% and 85% RH, the carbonation of C-S-H in the OPC/BFS paste seems to proceed at the higher RH.

3.6 Evaluation of phase assemblage by equilibrium analysis

For carbonated samples at 43%, 66% and 85% RH, the phase assemblage change due to carbonation was investigated by equilibrium analysis. Thermodynamic modeling predicts that the carbonation (dissolution) of C-S-H phase proceeds after portlandite is completely consumed (Shi et al. 2016). However, the carbonation of the C-S-H phase and portlandite was revealed to occur simultaneously under real exposure conditions (Groves et al. 1991). To take into account the behavior of real carbonation conditions, the consumed calcium hydroxide contents due to carbonation based on consumption ratio (Fig. 6) were used as the amounts of portlandite on equilibrium analysis. Thus, the conversion of portlandite on equilibrium analysis between CO2 and this initial phase assemblage allows for the assessment of the carbonation behavior of the C-S-H phase. The consumed contents of portlandite were determined by multiplying the portlandite contents of equilibrium analysis results, which calculated from the reaction amount of clinker minerals and BFS, by the consumption ratio, as shown in Fig. 6.

Figure 9 shows the change of carbonated phase assemblage and Ca/Si ratio of C-S-H by equilibrium calculation. The water content (H2O/Si ratio) of the C-S-H phase was accommodated to consider moisture conditions in non-carbonated samples at different RHs. In Fig. 9, the C-S-H phase formed the low Ca/Si ratio C-S-H (TobH: Ca/Si=0.66 for OPC, TobH: Ca/Si=0.66 for OPC/BFS) from the fast progress of carbonation of high Ca/Si ratio C-S-H (JenD: Ca/Si=2.25, JenH: Ca/Si=1.33, TobD: Ca/Si=1.25 for OPC, T5C: Ca/Si=1.00, T2C: Ca/Si=1.50 for OPC/BFS) on samples at 43% and 66% RH. The Ca/Si ratio of the C-S-H phase decreased with the progress of carbonation. The small amount of low Ca/Si ratio C-S-H on OPC paste at 85% RH formed. Besides, the Ca/Si ratio of the C-S-H phase also slightly decreased. For OPC and OPC/BFS, monosulphate at 43% and 66% RH decomposed on 91 days of carbonation. The formation of silica gel was not observed on all samples until 91 days of carbonation. The precipitation of aragonite was associated with silica gel formation (Black et al. 2007). The XRD chart in Fig. 7 and the quantitative value by Rietveld analysis show the small amount of aragonite. The predicted results by equilibrium analysis probably agree with the experimental results.

3.7 Change of microstructure due to carbonation

For pretreatment of water vapor sorption and nitrogen sorption measurements, samples were oven dried at 110ºC. The water in sample was removed while the hydration products are partially de-hydroxylated. The small pore, such as gel pore in C-S-H might be collapsed.

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**Fig. 8 Total amounts of calcium carbonate and decomposition ratio of C-S-H of (a) OPC and (b) OPC/BFS.**
(Juenger et al. 2001; Korpa and Trettin 2006; Snoeck et al. 2014). However, in this study, it seems possible to evaluate the relative effect of non-carbonation and carbonation. Figure 10 shows the water vapor sorption of carbonated samples on 91 days for OPC and OPC/BFS paste. In this section, two types of RHs (as percentage and as decimal) are shown. The RHs of the carbonation conditions are shown as percentages, and the RHs during water vapor sorption test are shown as decimals. Comparing carbonated samples at 43% and 85% RH, the water vapor sorption on a sample at 43% RH, which progressed the carbonation reaction, was smaller than that at 85% RH. The decrease of water vapor adsorption isotherms on carbonated samples has been reported in a previous study (Houst and Witmann 1994). The hysteresis of the adsorption and desorption scanning curve over RH=0.4 also decrease due to carbonation on OPC and OPC/BFS. At 43% RH, the sudden reduction of desorption scanning curve around RH=0.4 was not observed. The drop around RH=0.4 is correlated to the effect of ink-bottle pores or the removal of water molecules around calcium ions in the C-S-H (Maruyama et al. 2018). The water saturation degree of non-carbonated and carbonated samples on 91 days for OPC and OPC/BFS is shown in Fig. 11. For OPC paste at 43% RH, the water...
saturation degree on carbonated samples over RH=0.5 declined against the non-carbonated sample. Since the pore diameter at RH=0.5 was assumed to be about 3 nm according to the Kelvin equation, there is a possibility that the coarsening of pore structure out of 3 nm is occurring on the carbonated samples. Besides, the water saturation degree of the carbonated OPC/BFS paste at 43% RH was lower than that of the carbonated OPC/BFS across the whole range of RHs of the water vapor sorption test. Therefore, the water saturation degree of the carbonated OPC/BFS paste at 43% RH was lower than that of the carbonated OPC/BFS across the whole range of RHs of the water vapor sorption test. Thus, the microstructure of pores up to 3 nm was also influenced by the carbonation for OPC/BFS. This trend of decrease of water saturation degree was in agreement with the results of carbonated cement paste, including slag and fly ash shown in the previous research (Auroy et al. 2015). On the contrary, the water saturation degree of carbonated samples for OPC and OPC/BFS at 85% RH was coincident with the non-carbonated samples. These results were explained that all the pores with various pore size distribution were altered in a similar manner by carbonation.

Figure 12 shows the changes in the specific surface area of H$_2$O and N$_2$ on non-carbonated and carbonated samples on 91 days of carbonation.

### 4. Discussion

In the current study, there are significant changes in the carbonation rates of C-S-H and portlandite at different RHs. In other words, portlandite is easily carbonated at high RHs. As the RH decreases, the carbonation of C-S-H occurs more rapidly than that at high RHs. In the present paper, the carbonation level of C-S-H at 43% RH was higher than those at 66% and 85% RH (Fig. 8). In addition, the relation between carbonation shrinkage and calcium carbonate content showed different trend at RHs (Fig. 5). Therefore, the decomposition of C-S-H assessed the carbonation shrinkage strains for the OPC and OPC/BFS paste to investigate the effect of C-S-H carbonation. The decomposition ratio of the C-S-H phase, which was obtained by the equilibrium analysis, was calculated using the following Eq. (3). It should be noted that the decomposition ratio of the C-S-H phase calculated by Eq. (3) was used as a C-S-H volume in Fig. 9.

Figure 13 shows the relation between the carbonation shrinkage strain and C-S-H decomposition ratio on each carbonation time at 43%, 66% and 85% RH. In this figure, the filled and open symbols denote OPC paste sample and OPC/BFS paste sample, respectively. The specific surface area of H$_2$O and N$_2$ on OPC and OPC/BFS samples at 43%, 66% and 85% RH decreased due to carbonation. The decrease of specific surface area by water vapor of OPC/BFS samples at 43% and 66% RH were larger than OPC samples.
accompanied by the removal of calcium ion from C-S-H interlayer.

The MCL of the carbonated C-S-H phase was calculated from Richardson tobermorite model by using the Ca/Si ratio (Richardson 2014). Richardson’s tobermorite model was demonstrated for C-S-H in which the Ca/Si ratio is less than 1.5. The MCL change due to Ca/Si ratio obtained for Richardson model have been compared with some data from literature using \(^{29}\)Si MAS NMR (Kangni-Foli et al. 2020). At low Ca/Si ratios (Ca/Si ratio of 1 or less), this behavior is in line with literature data.

In the Richardson tobermorite-based structure model, MCL was calculated by Eq. (5).

\[
MCL = \frac{1 - v}{v} 
\]  

where \(v\) is the fraction of vacant sites in the aluminosilicate chains. The Ca/Si ratio was evaluated by using the fraction of vacant sites.

\[
\frac{Ca}{Si} = \frac{2}{3} + \frac{v}{1 - v} 
\]  

In this study, MCL of carbonated C-S-H was calculated by using the Ca/Si ratio that was obtained for the phase equilibrium analysis. Figure 14 shows the changes in carbonation shrinkage and MCL with decreasing the Ca/Si ratio of the C-S-H phase. The relation between carbonation shrinkage and the Ca/Si ratio of C-S-H was found to be independent of carbonation time, different RHs and types of the binder. The carbonation shrinkage increased rapidly below the Ca/Si ratio of 1.00 to 1.20. Besides, this correlation was good in agreement with the increase of MCL of the C-S-H phase. Hence, the carbonation shrinkage behavior at different RHs (Fig. 5) can be explained by the difference in carbonation progress of the C-S-H phase.

A previous study showed that the size of C-S-H and portlandite are different (Richardson 2004). Portlandite was the crystalline size of about 10 to 20 \(\mu\)m and formed in the coarse pore, such as capillary pore. The outer product of C-S-H exhibits the fibrillar morphology, which is about 100 nm wide, and the inner product of C-S-H compose aggregates of small globular particles, which were 4 to 6 nm in diameter. The carbonation process consists of dissolution and precipitation reaction. The water in the pore needs to occur carbonation as a reaction medium. The carbonation of portlandite at lower RH seems to retard progression because the water around portlandite crystals can evaporate. The protective film of calcium carbonate on portlandite crystals inhibits the subsequent carbonation reaction (Galan et al. 2015). Meanwhile, since the water in the gel pore of C-S-H remains in sufficient quantity at a low RH (Muller et al. 2013), the C-S-H phase is expected to occur the consecutive carbonation reaction at low RH.

The decrease of water vapor sorption isotherm and specific surface area was correlated with the decomposition of C-S-H due to carbonation. However, the trend of water saturation degree on carbonated samples at 43% RH was different for the results of non-carbonated samples (Fig. 11). This is because of the change of microstructure of carbonated C-S-H. The microstructure of C-S-H interlayer was evaluated by the specific surface area of water vapor (Feldman and Sereda 1968), while the results of the specific surface area of \(N_2\) appeared as the change of aggregability of C-S-H globule (Jennings 2000, 2004). The increase of inaccessible pore on \(N_2\) adsorption, which means the decrease of the specific surface area of \(N_2\), was explained by the development of aggregation of the C-S-H cluster (Maruyama et al. 2014).

Therefore, our results of the decrease of specific surface area on \(H_2O\) and \(N_2\) reflect the progressive polymerization in the interlayer and the development of ag-

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**Figure 13** Relation between carbonation shrinkage strain and C-S-H decomposition ratio on each carbonation period.

**Figure 14** Change in carbonation shrinkage and MCL with decreasing Ca/Si ratio of C-S-H phase.
gregation of C-S-H particle on micro-scale. These microstructural changes lead to the pore structure's coarsening in mesoscale, such as capillary pore, and the macro volume change by carbonation shrinkage. Since the carbonation shrinkage for OPC/BFS at 43% RH is larger than OPC, the carbonated samples at 43% RH on 91 days seemed that the decalcification and polymerization of C-S-H with low bulk Ca/Si ratio occur the change of microstructure from micro-scale to mesoscale.

This alteration of pore structure can be observed from the well-carbonated samples, including the C-S-H phase with the Ca/Si ratio up to 1.00 (Fig. 9). In Fig. 14, the mean chain length of the C-S-H phase on the Ca/Si ratio up to 1.00 is increasing quite rapidly. The microstructure of carbonated samples at 85% RH, including the C-S-H phase with the Ca/Si ratio of 1.00 appears to do not show a significant alternation.

5. Conclusions

In this study, the carbonation shrinkage, phase assemblage and microstructural change of hardened cement paste with and without BFS due to carbonation at 11%, 43%, 66% and 85% RHs were investigated. The development in the carbonation shrinkage during carbonation differed with the RH conditions even with almost the same calcium carbonate contents. The carbonation shrinkage for the OPC/BFS paste was larger than that for the OPC paste at the same RHs.

The XRD/Rietveld analysis results showed that calcite was the dominant mineral among the calcium carbonate polymorphs in the carbonation environment at 66% and 85% RH. In contrast, vaterite was formed as the main calcium carbonate polymorphs in carbonated OPC paste at 43% RH. For the OPC/BFS paste at 43%, 66%, and 85% RH, vaterite was precipitated as the calcium carbonate polymorphs. The relation between carbonation shrinkage and the decomposition ratio of C-S-H obtained by phase equilibrium analysis was independent of the carbonation progress and different RHs. The development in the carbonation shrinkage on all samples was in agreement with the increase of mean chain length during the decrease of the Ca/Si ratio of the C-S-H phase. The carbonation shrinkage of the OPC/BFS paste was largely affected by the decalcification of C-S-H because of the presence of C-S-H with a low Ca/Si ratio in the OPC/BFS paste.

The water vapor sorption and specific surface area by water and N2 were decreased with the progressive carbonation. From these results, the polymerization of silicate anion and the aggregation of C-S-H particles due to the decalcification of C-S-H appear to occur in the coarsening of mesoscale pore structure and the carbonation shrinkage. This microstructural alternation was observed from the well-carbonated samples, including the C-S-H phase with the Ca/Si ratio under 1.00.

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