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Scientific paper

Impact of TiO₂ Nanoparticles on Drying Shrinkage of Hardened Cement Paste

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Abstract

This paper reports the influence of nano-TiO₂ on hydration reactions and drying shrinkage behavior during the first drying process of hardened cement pastes. Cement pastes containing 3 wt% nano-TiO₂ (by external addition) in cement and reference samples were prepared with water to cement ratios (W/C) of 0.40 and 0.55. The results of experiments on samples hydrated for 6 months show that in the mature state of hydration, the addition of TiO₂ retards the reaction of belite and slightly reduces the precipitation of portlandite in both W/C ratios. Regarding the formation of C-S-H, the addition of TiO₂ increases the mean chain silicate length in C-S-H in the saturated state, and nano-TiO₂ is present in the vicinity of low density (LD) C-S-H during the hydration process. The drying shrinkage of the cement paste with nano-TiO₂ in the first drying process is larger than the reference sample when W/C = 0.55, but the opposite occurs when W/C = 0.40. This is explained by the increased precipitation of low density C-S-H due to the addition of nano-TiO₂ when W/C = 0.55; however, when W/C = 0.40 the amount of LD C-S-H in the sample with nano-TiO₂ does not increase due to their being less space for precipitation in the sample.

1. Introduction

Titanium dioxide (TiO₂) is chemically stable and photoactive, making it a popular material in industry and the field of engineering. For the past 30 years, TiO₂ photocatalyst technology has been developed, and attempts have been made to apply this material for construction and building materials with self-cleaning, air or water purification, and antibacterial functions (Ohama and Germert 2011).

Nanoparticles having a diameter of 1 ~ 100 nm are not only small in size, the compounds physical and chemical properties are significantly different than the same compound with a particle size of several hundred nanometers or more. With the development of nanotechnology, TiO₂ nanoparticles with an anatase type crystal structure, which are expected to be the most effective photocatalyst for enabling industrial applications, have been used as an admixture for concrete in recent decades.

Some investigations have revealed that nano-TiO₂ influences not only depollution and self-cleaning performance, but it also improves the inherent properties of hardened cement pastes (Chen et al. 2012; Meng et al. 2012; Feng et al. 2013; Yang et al. 2015; Li et al. 2017). Chen et al. investigated blending nano-TiO₂ into cement pastes and mortars to determine their effect on hydration and properties of the hydrated cement pastes. Through their experimental studies, the addition of nano-TiO₂ powders significantly accelerated the hydration rate and promoted the degree of hydration of the cementitious materials at early ages (Chen et al. 2012). Further, during the hydration process, nano-TiO₂ was inert and stable, so TiO₂ was confirmed to be a non-reactive fine filler that acts as potential nucleation sites for the hydration products. It is suggested that the addition of TiO₂ causes changes in microstructure. Feng et al. revealed that, by admixing nano-TiO₂ into cement, nano-modification increased the amount of cementitious phase in the paste, decreased the micro-porosity and amount of internal micro-cracks and defects, formed a denser microstructure, and led to the formation of needle-shaped nanoprecipitates (Feng et al. 2013).

In addition, the admixing of nano-TiO₂ into cement enhances the compressive and flexural strengths (Nazari and Riahi 2010; Chen et al. 2012; Feng et al. 2013; Yang et al. 2015). This is assumed to be due to a greater formation of hydration products and denser microstructure in the presence of nano-TiO₂.

However, data on the influence of the addition of nano-TiO₂ on the drying shrinkage of hardened cement paste or concrete is scarce. Hasebe and Edahiro measured the drying shrinkage strain of concrete mixed with nano-TiO₂ in various proportions, and the specimens mixed with nano-TiO₂ generally tended to shrink more than the reference sample (Hasebe and Edahiro 2014). An experimental study on the effect of TiO₂ on the shrinkage behavior of hardened cement paste was conducted in the range of up to an age of 28 days and includes the effects of the autogenous shrinkage (Land
As discussed, previous studies on the addition of nano-TiO₂ have been mainly focused on its effect on the hydration process at early ages or morphology and crystal structures of precipitated products. Therefore, we concluded that little research has been conducted on the impact of microstructure in mature paste, especially for the first drying process, and such research is required to achieve commercial application.

Our research focuses on understanding the influence of nano-TiO₂ on the drying shrinkage of hardened cement pastes, especially during the first drying process. Reference samples (plain) and samples containing 3 wt% nano-TiO₂ (by extra-addition) in cement were prepared. After almost full hydration was obtained by curing the samples in lime saturated water for 6 months, powder X-ray diffraction (XRD) and Rietveld analysis, morphological observation using field emission-scanning electron microscopy, and solid state ²⁹Si nuclear magnetic resonance measurements were conducted in order to evaluate the impact of TiO₂ on the hydration process. In addition, short-term length change isotherms for samples dried under different relative humidities at 20ºC and water vapor/nitrogen sorption isotherms were obtained. Based on these experimental results, we describe the impact of TiO₂ on the shrinkage behavior of hardened cement paste.

2. Experimental method

2.1 Materials

White Portland cement whose density is 3.05 g/cm³ and Blaine value is 3420 m²/g was used for the cement paste binder. The chemical compositions, and mineral compositions of white Portland cement are shown in Tables 1 and 2, respectively. The mineral compositions were determined by XRD measurements and Rietveld analysis.

Nano-TiO₂ particles (anatase type, provided by the Tayca Corporation) were used in the experiments. The TiO₂ suspension was dried for 1 week so that powder state nano-TiO₂ was used to prepare test specimens. The SEM image of dried nano-TiO₂ powder is shown in Fig. 1. Nanoparticles are spherical in shape with a diameter of approximately 50 nm.

The water-cement ratios of cement pastes were 0.40 and 0.55. Reference samples which do not contain nano-TiO₂ were named W40-Plain and W55-Plain. Specimens with 0.40 and 0.55 W/C containing nano-TiO₂ were named W40-TiO₂ and W55-TiO₂, respectively. The amount of nano-TiO₂ powder externally added to the cement was 3.0% by mass of cement for each W/C condition. Cement paste (ca 300 g) was mixed in a 500 cc vacuum mixer for 3 min after water was added. To disperse TiO₂ particles in the sample and avoid agglomeration, 1.5 min of sonication was applied for samples W40-TiO₂ and W55-TiO₂. Then, the pastes were scraped and mixed for a further 3 min by the mixer. All the materials were stored in a thermostatic chamber at 20 ± 1ºC for 1 day prior to mixing. The mixing was performed at room temperature (ca 20ºC), and the specimens were then immediately returned to a thermostatic chamber. To minimize segregation, cement pastes were remixed every 30 min for 6 hours. After remixing, the specimens were placed into vials with Φ15 mm and 80 mm depths, and they were stored in a thermostatic chamber. They were demolded after 4 days, and samples were immersed in lime-saturated water at 20 ± 1ºC for 6 months.

2.2 Measurements

Table 3 shows a list of experiments and test specimens. After 6 months of curing, two water content conditions were used for each W/C ratio; one was dried for more than a month in a desiccator with an 11% relative humidity using lithium chloride saturated solution, and the other was kept in a saturated state.

![Fig. 1 SEM image of nano-TiO₂ particle.](image-url)
Morphological observations of fracture surfaces of cement pastes were measured at each condition. Three samples were crushed and then dried and degassed at 105ºC for 2 weeks at a constant temperature of 20 ± 1ºC in a desiccator using circulated air scrubbed with a CO₂ absorbent and a saturated LiCl aqueous solution (11% RH). After drying, the samples were ground in a ball mill and graded with a 90 μm sieve, and only the powder that passed through the sieve was used for the various measurements. XRD measurements were conducted under the following instrument conditions: Cu-Kα X-ray source, 40 kV tube voltage, 40 mA tube current, 2θ = 2 ~ 65º scanning range, 0.02º step width, and 0.5º/min scanning speed. The samples whose hydration reaction was stopped by acetone, the samples were dried for 2 weeks at a constant temperature of 20 ± 1ºC in a desiccator using circulated air scrubbed with a CO₂ absorbent and a saturated LiCl aqueous solution (11% RH). After drying, the samples were ground in a ball mill and graded with a 90 μm sieve, and only the powder that passed through the sieve was used for the various measurements. XRD measurements were conducted under the following instrument conditions: Cu-Kα X-ray source, 40 kV tube voltage, 40 mA tube current, 2θ = 2 ~ 65º scanning range, 0.02º step width, and 0.5º/min scanning speed. The samples whose hydration reaction was stopped and then underwent humidity conditioning were admixed with 10 wt% corundum (α-Al₂O₃) as an internal standard. Rietveld analysis was done for the entire measured spectrum using the TOPAS ver. 4.2 software (Bruker AXS). Alite (C₃S), belite (C₂S), aluminate phase (C₃A), ferrite phase (C₄AF), periclase (MgO), calcite (CaCO₃), gypsum (CaSO₄·2H₂O), basanite (CaSO₄·0.5H₂O), portlandite (Ca(OH)₂ (CH)), ettringite (Ca₄A·3CaSO₄·32H₂O (Ett)), monosulfate (C₃A·CaSO₄·12H₂O (Ms)), hydrogarnet (C₃A·3CaSO₄·12H₂O (Hg)), hemicarboaluminate (C₃A·0.5CO₂·12.5H₂O), and monocarbonate (C₃A·CO₂·12H₂O), as minerals and cement hydration products, were chosen to be quantified; α-Al₂O₃ (10 wt%) was admixed with the analysis sample as an internal standard. The details of the XRD/ Rietveld analysis are described in our previous paper (Maruyama and Igarashi 2014, 2015). Three samples were measured at each condition.

(2) FE-SEM
Morphological observations of fracture surfaces of cement pastes were performed using secondary electron images (SEI) from a field emission-scanning electron microscope (FE-SEM (JSM-7500FA, JEOL)). The samples were crushed and then dried and degassed at 105ºC for 30 min using a vacuum pump (ultimate pressure performance: 6.7 × 10⁻² Pa) and heating mantle. In addition, an osmium coating was applied to the dried sample to compensate for the electrical charge during observation.

(3) Short-term length change isotherm (SLCI)
For measuring SLCI, 3 × 3 × 1 mm samples were cut from saturated specimens for use with a more rapid experimental technique in which these small specimens were subjected to forced drying under an RH-controlled air flow. SLCI for samples were measured using a thermomechanical analyzer (TMA) coupled with an RH generator (TMA4000SA and HC9700, Bruker AXS). Length changes were measured with a linear variable differential transfer (LVDT) with a minimum resolution of 0.025 μm and a contact load of 0.098 N. The samples were incrementally dried from the saturated state to 5% RH, after which they were incrementally re-humidified back to 90% RH. All the processes were conducted at 20 ± 0.1ºC. For each step, the RH of the atmospheric flow was kept constant for 5 h.

(4) 29Si-NMR
29Si Dipolar Decoupling (DD) MAS NMR spectra were acquired using a Bruker Avance 300 MHz spectrometer equipped with a 9.4 T wide bore magnet. Samples were packed into 7 mm ZrO₂ rotors and rotated at MAS rates up to 5 kHz using a standard CP MAS probe. Generally, a 60 sec recycle delay was used, and a number of scans were 2000 times. All spectra were recorded at room temperature and referenced to the hexacyclotrisiloxane peak at -9.55 ppm relative to tetramethylsilane (run separately).

During measurements, the samples were kept in their initial condition (i.e. in the saturated condition), so they contained evaporable water. In order to compare spectra between samples, the measured signals were normalized to the mass of a sample dried at 1000ºC.

The chemical shift values of Q₀, Q₁, Q₂, Q₂(H₂O) and Q₃ were assumed to be -69.6 to -73.5, -75.6 to -79.0, -82.0, -85.0, and -91.5 to -92.3 ppm, respectively, based on the shifts reported in Brunet et al. (2004) and Rawal et al. (2010). The peaks were decomposed assuming a Gaussian distribution. The mean chain length (MCL) of C-S-H in C-S-H were calculated using the following equation (Skibsted and Andersen 2013; Richardson 2014):

| Parameter | Dried condition | XRD | SEM | Si-NMR | SLCI | Water vapor sorption | Nitrogen sorption |
|-----------|-----------------|-----|-----|--------|------|---------------------|------------------|
| W40-Plain | saturated       | ○   | -   | ○      | ○    | ○                   | ○                |
|           | 11%RH           | -   | -   | -      | -    | -                   | -                |
| W40-TiO₂  | saturated       | ○   | -   | ○      | ○    | ○                   | ○                |
|           | 11%RH           | -   | -   | -      | -    | -                   | -                |
| W55-Plain | saturated       | ○   | -   | ○      | ○    | ○                   | ○                |
|           | 11%RH           | -   | -   | -      | -    | -                   | -                |
| W55-TiO₂  | saturated       | ○   | -   | ○      | ○    | ○                   | ○                |
|           | 11%RH           | -   | -   | -      | -    | -                   | -                |

Table 3 List of measurement variables and test specimen.
\[ \text{MCL} = \frac{2(Q_i + Q_1 + 1.5Q_{2(1.45)})}{Q_i} \]  

(1)

(5) Water vapor sorption measurement
Water vapor sorption measurements were conducted by the volume method using a water vapor sorption analyzer (Hydrosorb 1000, Quantachrome). The ~20 mg samples used for measurements were at 20\(^\circ\)C, with a pressure tolerance of 0.05 mmHg and a time tolerance of 120 sec. Adsorption and desorption branches were measured at \(p/p_0\) intervals of 0.05 up to 0.95 and ended at 0.98 (RH = 98%). The specific surface area \(\left(S_{\text{H}_2\text{O}}\right)\) of the adsorption branch was calculated using BET theory with a water molecule section value of 0.114 \(\text{nm}^2\) (Mikhail and Selim 1966). The samples were crushed, and powder with a particle size of 25 – 75 \(\mu\)m was used for this analysis. For pre-treatment, the samples were dried using a vacuum pump (theoretical minimum pressure of \(6.7 \times 10^{-2}\) Pa) and heated to 105\(^\circ\)C with a heating mantle for 30 min; this led to the very dry initial state (shown for convenience as 0% RH) used in the sorption isotherm graphs.

(6) Nitrogen sorption measurement
Nitrogen sorption tests were performed by the volume method using a nitrogen sorption analyzer (BELSORP-mini II, MicrotracBEL Corp.). An ~100 mg sample was used for each measurement at 77.4 K, with a sorption tolerance of 5.0 \(\text{cm}^3/\text{g}\) and a time tolerance of 180 sec. The specific surface area \(\left(S_{\text{N}}\right)\) of the adsorption branch was calculated using BET theory with a nitrogen molecule section value of 0.162 \(\text{nm}^2\) (McClellan and Harnsberger 1967). The samples used in this measurement were powder classified in the same way as the water vapor sorption test samples; the samples were dried using a vacuum pump (theoretical minimum pressure of \(6.7 \times 10^{-2}\) Pa) and heated to 105\(^\circ\)C with a heating mantle for 30 min.

3. Experimental results

3.1 Impact on hydration
After curing in lime saturated water for 6 months, the degrees of hydration and phase composition of cement paste were measured using XRD / Rietveld analysis. Figure 2 shows degrees of hydration of each clinker and the average for the sample. The degree of hydration of C\(_3\)S (alite) was approximately equal in the samples with and without TiO\(_2\) for each W/C ratio, and C\(_3\)A (aluminate phase) was fully hydrated in all cases. However, for C\(_2\)S (belite) the degree of hydration of TiO\(_2\) added sample was significantly lower than that of the Plain sample for each W/C ratio. Therefore, this shows that nano-TiO\(_2\) particles delay the reaction of belite in the case of long-term hydration periods (e.g. cured in lime saturated water for 6 months). In Fig. 3, the mass ratios of amorphous phase and portlandite to 1.0 g of anhydrous cement paste are shown. The amount of amorphous phase, in which C-S-H was expected to be the major component, was approximately equal for samples with and without TiO\(_2\) at each W/C ratio, but the amount of portlandite in the sample with TiO\(_2\) was slightly lower than that of the Plain sample for each W/C ratio. It has been reported that TiO\(_2\) has no pozzolanic reactivity during the hydration reaction (Chen \textit{et al.} 2012), so the depression of portlandite precipitation due to the addition of nano-TiO\(_2\) was confirmed. One reason of this depression of precipitated amount of portlandite comes from the retardation of reaction of belite due to the addition of nano-TiO\(_2\).

![Fig. 2 Degree of hydration determined by XRD/Rietveld analysis. Samples were measured after curing in lime saturated water for 6 months.](image)

![Fig. 3 Mass ratio of amorphous phase/portlandite in the anhydrous cement paste.](image)
The mean chain silicate length (MCL) of C-S-H was calculated from Eq. 1, and the results are shown in Fig. 7. The MCL of the sample with TiO₂ is larger than that of the Plain sample for each W/C ratio; this proves that the addition of TiO₂ changes the structure of precipitated C-S-H.

Figure 8 shows secondary electron images obtained by FE-SEM to observe the morphology of cement paste. The sample used for SEM observation was dried at 20°C, 11% RH for 1 month after 6 months of water curing. Figures 8 (A) and 8 (B) are images of W55-Plain and W55-TiO₂, respectively, focusing in the vicinity of LD C-S-H. Figure 8 (C) is an enlarged view of the white outlined rectangular area shown in Fig. 8 (B). TiO₂ particles were present, as shown by white outlined circles in Fig. 8 (C), and it was confirmed that the TiO₂ particles are present in the vicinity of LD C-S-H during and after hydration. Li et al. (2017) examined synthesized C-S-H with nano-TiO₂ using transmission electron microscopy (TEM) and reported the existence of a nanocrystalline region inside C-S-H. The area of the nanocrystalline region is comparable to that of the TiO₂ nanoparticles, which also indicates that nano-TiO₂ works as a nucleus for hydration products.

3.2 Drying shrinkage and adsorption properties
Short-term length change isotherms in the first drying and re-adsorption processes are shown in Fig. 9. In the first drying process, no difference was found in the drying shrinkage strain between samples with and without...
TiO₂ for each W/C ratio in the range from the saturated state to 60% RH. Weiss et al. (2008) and Maruyama et al. (2016) reported about long-term or short-term drying shrinkage of hardened cement paste with/without shrinkage reducing admixture (SRA) under first drying process. At higher relative humidity (e.g. above 90% RH for long-term drying and above 80% RH for short-term drying), drying shrinkage strains of plain and SRA mixed sample were almost the same. In this RH range, water evaporate from the larger pores (capillary pore) of cement paste. Therefore, shrinkage due to capillary tension is not a dominant factor in drying shrinkage of hardened cement paste. As for our results, the effect by nano-TiO₂ does not appear in shrinkage according to capillary tension.

At 60% to 40% RH, a difference in shrinkage appeared; shrinkage in the Plain sample was greater than in the TiO₂ sample when W/C = 0.40, but TiO₂ showed greater shrinkage when W/C = 0.55. Below 40% RH, the difference in shrinkage was approximately equal to the value at 40% RH. Therefore, although the influence on the shrinkage strain due to the addition of nano-TiO₂ varies depending on the W/C ratio, it was clearly proven that changes occur in the cement paste in the first drying process from 60% to 40% RH at 20°C. Changes between the saturated state to 40% RH in the first drying process were predominantly due to low density (LD) C-S-H (Maruyama et al. 2014). It should be noted that
definition of LD C-S-H follows two types of C-S-H classified by nitrogen sorption (Tennis and Jennings 2000). Haji et al. (2016) evaluated the relationship between drying shrinkage and amount of two types of C-S-H using experimental data of ordinary Portland cement paste. Based on their results, drying shrinkage caused by LD C-S-H is about 1.67 times larger than that by high density C-S-H with assuming that all of drying shrinkage strain of hardened cement paste is caused by the alteration of C-S-H. Therefore, it is thought that addition of TiO₂ influences the morphology alteration of this LD C-S-H.

In the re-adsorption process, the difference in shrinkage between the samples with and without TiO₂ was relatively small at the final 90% RH, but the influence of TiO₂ on the shrinkage behavior in the re-adsorption process was negligible.

Water vapor sorption isotherms are shown in Fig. 10, and the BET surface area (S_{H₂O}) calculated from the adsorption branches are shown in Fig. 11. The measured samples were in a saturated state after curing in lime-saturated water for 6 months. When W/C = 0.40, the shapes of the adsorption branches for the Plain and TiO₂ samples were almost identical. In the case of W/C = 0.55, the adsorption for W55-TiO₂ was lower than that of Plain when above 60% RH in the adsorption branch and above 30% RH in the desorption branch; this means that the mesoscale pore structure is changed by the addition of TiO₂ for W/C = 0.55, but it was not clearly seen in W/C = 0.40 case. In Fig. 11, the S_{H₂O} of the sample with TiO₂ was slightly larger than that of Plain for each W/C ratio.

Nitrogen sorption isotherms measured on a saturated sample and on a sample which was dried at 11% RH (20°C) for 1 month are shown in Fig. 12. In the saturated state sample with W/C = 0.40, W40-TiO₂ had less sorption than W40-Plain over the full range of relative pressure. When W/C = 0.55, W55-TiO₂ had more sorption than W55-Plain when P/P₀ ≤ 0.8, but less sorption than Plain when P/P₀ > 0.8. In the samples dried at 11% RH, the amount adsorbed for the samples with and without TiO₂ were approximately equal at a relative pressure lower than 0.8 for each W/C ratio. The specific surface areas (S_{N₂}) calculated from the adsorption branches are shown in Fig. 13. In the saturated state, the S_{N₂} of Plain was larger for a W/C = 0.40, and that of TiO₂ was larger at W/C = 0.55. After drying at 11% RH, S_{N₂} was independent of TiO₂ addition for each W/C ratio.

In general, adsorption of nitrogen molecules to cement paste is controlled by LD C-S-H (Jennings and Tennis 1994; Tennis and Jennings 2000). Therefore, the S_{N₂} has a correlation with the amount of LD C-S-H.

From the nitrogen sorption results, addition of TiO₂ increased the amount of LD C-S-H accessible to nitrogen at W/C = 0.55. In the case of W/C = 0.40, the proportion of LD C-S-H was not increased by the addition of TiO₂, but rather was less than Plain.

4. Discussion

TiO₂ nanoparticles dispersed in cement paste act as nuclei for hydration products without pozzolanic activity during the hydration process and retard the reaction of belite in the mature hydrated state while changing the amount of C-S-H precipitated and the pore structure formed.

However, the effect on drying shrinkage strain during the first drying process varies depending on the W/C ratio. At W/C = 0.40, the amount of LD C-S-H in the sample containing TiO₂ decreases, and the drying
shrinkage becomes less than that of the Plain sample in the first drying process. When W/C = 0.55, the amount of precipitated LD C-S-H increases with the addition of TiO$_2$, and the drying shrinkage during the first drying is greater than the Plain sample.

That is, in the case of W/C = 0.55, a greater amount of LD C-S-H is precipitated around TiO$_2$ nanoparticles during the hydration process, in which TiO$_2$ acts as the nucleus for hydration products. However, when W/C = 0.40, the distance between cement particles is small, and the space where LD C-S-H with lower density than the inner C-S-H can be precipitated is limited in comparison with higher W/C ratios (e.g. 0.55). Therefore, when TiO$_2$ is added, the proportion of LD C-S-H remains lower than the Plain sample; as a result, it is thought that drying shrinkage is reduced.

Based on Tennis and Jennings model (T-J model), the ratio of the mass of LD C-S-H to the total mass of C-S-H ($M_r$) can be calculated by (Tennis and Jennings 2000):

$$M_r = \frac{S_{N2} M_D}{S_{LD} M_t}$$

where $S_{N2}$ is the specific surface area of the dried paste measured by nitrogen sorption, $M_D$ is the mass of dried paste, $S_{LD}$ is the surface area (m$^2$/g-dried LD C-S-H), and $M_t$ is the total mass of C-S-H. $S_{N2}$ is not independently measurable in nitrogen sorption, so it is assumed $S_{LD}$ for this study is the same as the fitting value reported by Tennis and Jennings (i.e. 247 m$^2$/g-dried LD C-S-H) (Tennis and Jennings 2000).

Figure 14 shows the calculated values of $M_r$ for each case. In W/C = 0.55, the $M_r$ of W55-TiO$_2$ is clearly larger than Plain. However, for W/C = 0.40, the $M_r$ of W40-TiO$_2$ is slightly lower than Plain. In this study, the addition of nano-TiO$_2$ in the W/C = 0.40 samples had little effect on the formation of LD C-S-H. In addition, this result is consistent with measured $S_{N2}$ shown in Fig. 13. The structure of LD C-S-H is more open and easy to lose the water than the HD C-S-H in the drying condition (Jennings and Tennis 1994; Maruyama et al. 2014). Therefore, the larger $M_r$ may also indicate the larger microstructural change of C-S-H during the first drying. As a result, it is thought to cause larger drying shrinkage, described in section 3.2 (Haji et al. 2016).

5. Conclusion

The impact of the addition of nano-TiO$_2$ particles on
hydration and drying shrinkage of hardened cement paste was investigated through comparison of a reference white cement paste with samples containing an additional 3.0 wt% nano-TiO$_2$ particles in cement after being cured in lime saturated water for 6 months. The new findings from the experiments include:

(1) In the mature state of hydration, such as following submerged curing for 6 months, the addition of TiO$_2$ retards the reaction of belite and slightly reduces the precipitation of portlandite as compared with Plain.

(2) In the saturated state, it was found that the mean chain length of Si in C-S-H calculated from $^{29}$Si-NMR was increased by the addition of TiO$_2$. In addition, it was confirmed by SEM observation that TiO$_2$ nanoparticles were present in the vicinity of low density C-S-H during the hydration process.

(3) In the first drying process, the drying shrinkage strain of the sample with TiO$_2$ (3.0 wt%) increased at W/C = 0.55 and was lower when W/C = 0.40. In addition, the influence of nano-TiO$_2$ on the shrinkage behavior appears mainly between 60% to 40% RH during the first drying process.

(4) From the nitrogen sorption measurements of the saturated state samples, the BET surface area of the sample with TiO$_2$ is greater than that of Plain when W/C = 0.55, but it was lower than Plain when W/C = 0.40. Therefore, it is suggested that the addition of TiO$_2$ increases the amount of low density C-S-H, and as a result, the drying shrinkage strain during the first drying process increases for W/C = 0.55. On the other hand, for W/C = 0.40, since the distance between cement particles is smaller than in the high W/C ratio case, and the space where low density C-S-H can be precipitated is limited, it suggests that the amount of low density C-S-H does not increase even when TiO$_2$ is added.

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