Temperature Dependency of Short-Term Length-Change and Desorption Isotherms of Matured Hardened Cement

Ippei Maruyama1* and Jiří Rymeš2

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Abstract
Short-term length-change isotherms and desorption isotherms of matured hardened cement paste were measured at different temperature conditions, namely, 20, 30, 40, 50, and 60°C. For the short-term length-change isotherms, higher temperature conditions resulted in a smaller drying shrinkage. This trend was largely controlled by the microstructural reorganization of the calcium-silicate-hydrates in the cement paste at elevated temperatures. The experimental results suggest that a portion of the evaporable water did not contribute to the shrinkage. In addition, based on the relationships between the incremental strain and the incremental evaporable water content, with a starting relative humidity of 5%, consistent trends were observed for the incremental strain and the incremental evaporable water when the incremental evaporable water content was less than 0.08 g/g-dried hcp. The microstructural reorganization pathways for elevated temperature and/or for drying were confirmed to be identical.

1. Introduction
Alteration of the material and strength properties of reinforced concrete members is induced by the drying and resultant shrinkage of hardened cement paste (hcp) in the concrete member. This shrinkage induces visible cracks when contraction of the concrete member is restrained by rebar and other structural members. These cracks may change the durability of the reinforced concrete members by allowing chemical penetration and thus leading to rebar corrosion. At the same time, the Young’s modulus of concrete is reduced due to the shrinkage of the hcp, which is greater than that of the aggregate, being restrained by the aggregate; the formation and expansion of the resultant cracks causes a reduction of the concrete load bearing section (Maruyama 2016). The stiffness of concrete members is crucial for maintaining structural integrity during earthquakes, and, consequently, effective aging management of concrete structures relies upon the determination of the rate of drying as well as the hcp shrinkage behavior.

Even though over the previous half-century a significant volume of research has been performed on the hcp shrinkage and drying mechanism (Powers 1965; Feldman 1968; Wittmann 1968; Bažant 1972; Bentur et al. 1979; Hansen 1987; Beltzung and Wittmann 2005; Maruyama 2010), the overall shrinkage behavior is not well understood. Interestingly, the drying shrinkage of the hcp at different temperatures is scarcely reported (Numao and Mihashi 1991; Maruyama and Kishi 2011). Yang et al. (2014) investigated the shrinkage behavior observed for young concrete samples with water-to-cement ratios (w/c) of 0.4 and 0.5, and they found a decreased final shrinkage with increasing temperature. Unfortunately, the effect of elevated temperatures was not isolated since the specimens were subjected to drying at a young age (1 day). The aim of this study is to provide new insights for the shrinkage mechanism by measuring and examining the short-term length-change isotherms (SLCI) at different temperature conditions.

2. Experimental method
The test specimens were based on a white Portland cement, with the chemical composition as shown in Table 1 (Maruyama et al. 2014, 2015, 2017). The w/c ratio was 0.55 and the paste (10 L) was mixed in a 20 L Hobart mixer for three minutes. After the water was added, the paste was further mixed for three minutes and scraped from inside the mixer. To minimize segregation, the paste was mixed again every 30 minutes over six hours to obtain a creamy consistency. It was then cast into a set of φ50 mm × 100 mm cylindrical molds, which were covered by polyvinylidene-chloride wraps and wet papers to avoid water loss from the specimens. The molds were placed in a thermostatic chamber at a temperature of 20 ± 1°C. They were demolded after 4 days and immediately immersed in lime-saturated water, where they were kept for 3 years at 20°C. After this long curing period, they were assumed to be almost fully hydrated.

To measure the SLCIs, samples with dimensions of 3 mm × 3 mm × 1 mm were cut from the central part of the demolded cylindrical samples and stored at the measurement temperature for one week in lime-saturated water. These small specimens were subjected to forced
drying in a relative humidity (RH)-controlled airflow. Length-change isotherms for samples dried at different RHs were obtained with a thermomechanical analyzer (TMA) coupled with an RH generator (AXS TMA4000SA and HC9700, Bruker). Length changes were measured with a linear variable differential transformer (LVDT) with a resolution of 25 nm and a contact load of 0.098 N. The experiments started at 90% RH at the measuring temperature, and then the samples were incrementally dried until they attained the minimum drying condition of 5% RH. The holding time for each step was eight hours. This holding time is based on previous experiments (Maruyama et al. 2015) in which the sample deformation is measured at 20°C. It should be noted that the complete equilibrium cannot be obtained after a holding time of one month. The data based on a holding time of eight hours will produce more than 85% of the estimated equilibrium strain, and the authors of this study considered the results to reasonably contribute to scientific discussion. The applied measurement temperatures were 20, 30, 40, 50, and 60°C. An example of the obtained results is shown in Fig. 1(a).

To measure the short-term desorption isotherms, a similar sample size as that employed for the SLCIs was used. The desorption isotherms at different temperatures were obtained with a thermogravimetry analyzer (TGA) coupled with an RH generator (2000SA and HC9700, Bruker AXS). The same RH and temperature histories as those used for SLCIs were applied. An example of the obtained results is shown in Fig. 1(b).

3. Experimental results

The SLCIs obtained at different temperatures are shown in Fig. 2. The SLCI is composed of two regions: the RH range from 100% (saturated condition) to 40%, and the RH range from 40% to 5%. The higher RH range (especially 80% RH – 40% RH) in which irreversible shrinkage occurs (Maruyama et al. 2018a) shows a larger temperature dependency: shrinkage becomes smaller when the drying temperature is higher. This trend is contrary to that found in the work of Numao and Mihashi (1991). This may be due the difference in the starting condition, namely, the sample was conditioned at the measuring temperature for one week prior to starting the test in this study, while they heated the samples without any pretreatment. Figure 3 shows the short-term shrinkage temperature dependency at 40% RH. As can be observed, from 20°C to 30°C, the shrinkage difference was quite large. Subsequently, the shrinkage at 40% RH gradually decreased and at 60°C, the total shrinkage was about 40% of that at 20°C. Concerning the low RH region also, a temperature dependency was found; however, the dependency was not significant, as shown in Fig. 4.

As a result of expansion found from 40% RH to 35% RH.

### Table 1 White cement chemical composition obtained from X-ray fluorescence elemental analysis*

<table>
<thead>
<tr>
<th>Ig. loss (%)</th>
<th>SO2 (%)</th>
<th>Al2O3 (%)</th>
<th>Fe2O3 (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SO3 (%)</th>
<th>Na2O (%)</th>
<th>K2O (%)</th>
<th>TiO2 (%)</th>
<th>P2O5 (%)</th>
<th>MnO (%)</th>
<th>Cl (%)</th>
<th>SUM</th>
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<tr>
<td>2.93</td>
<td>22.43</td>
<td>4.67</td>
<td>0.16</td>
<td>65.69</td>
<td>0.98</td>
<td>0.98</td>
<td>0.00</td>
<td>0.07</td>
<td>0.17</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>99.64</td>
</tr>
</tbody>
</table>

*Conducted by Taiheiyo Cement Corporation.

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Fig. 2 The initial short-term length-change isotherms of matured hardened cement paste at different tempera-

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Fig. 1 Examples of data obtained using (a) RH-TMA and (b) RH-TG.
(the details of this expansion is discussed in a previous reference (Maruyama et al. 2015)) and a differing dominant mechanism from those above 40% RH, an incremental shrinkage from 35% RH to 5% was investigated. The results are presented in Fig. 4. The incremental shrinkage from 35% to 5% RH at 60°C was approximately 75% of that at 20°C. While a large difference of 40% in shrinkage was found between 20°C and 30°C, a sudden drop was observed from 30°C to 40°C. In terms of short-term shrinkage, a large discrepancy was found between 20°C and 40°C.

The obtained desorption isotherms are summarized in Fig. 5. At the saturated state (100% RH in the figure), the results of water content are scattered. However, the overall trend was consistent: at lower temperatures, the hcp contained a larger amount of evaporable water at the same RH. The mechanism of the sudden drop (hereafter referred to as the kink) around 40% RH at 20°C has been discussed in prior studies (Brunauer et al. 1967; Baroghel-Bouny 2007; Maruyama et al. 2015, 2018a). The results presented in Fig. 5 may aid in providing clarification for the kinking mechanism, which is considered the result of a water vapor cavitation phenomenon. Recently, the water vapor cavitation phenomenon during short-term desorption has been studied by several investigators (De Burgh et al. 2016; Maruyama et al. 2018a) and experimentally confirmed by Maruyama et al. (2018b). The position of this kink shifted to a higher relative humidity as the temperature increased: 35% RH (20°C), 45% RH (30°C), 45% RH (40°C), and 50% RH (60°C). From Fig. 5, the kink location cannot be clearly observed for 50°C. The desorption isotherms also showed a different evaporable water content for the RH region below this kink. The evaporable water content barely changed from 40% RH to 5% RH for 40, 50, and 60°C. The temperature dependence of the water content at 5% RH is summarized in Fig. 6, where a sharp decrease to 50°C is evident. These trends are consistent with other long-term sorption isotherm results at different temperature conditions (Poyet 2009; Poyet and Charles 2009; Brue et al. 2012; Ben Abdelhamid et al. 2016; De Burgh and Foster 2017).

4. Discussion

Based on the experimental results, it can be observed that temperature largely influences the first-desorption isotherms as well as the length-change isotherms. Some studies have argued that the moisture content in the hcp dominates the shrinkage behavior (Powers 1965; Feldman 1968; Wittmann 1968; Bažant 1972; Beltzung and Wittmann 2005; Maruyama 2010); however, they failed to explain the role of microstructure reorganization during drying. Figure 7 shows the relationship between the incremental strain (dS) and the incremental evaporable water (dW) for different temperature conditions. The results of Fig. 7 are for the 5% RH condition at the given temperature conditions. For dW ranging 0 – 0.08
g/g-dried hcp, $\text{dS}$ as a function of $\text{dW}$ shows consistent results. Nevertheless, the evaporable water content at 5% RH at different temperatures is different, as shown in Fig. 6. For $\text{dW}$ greater than 0.08 g/g-dried hcp, three different trends are observed: (1) the strains at 20°C show the largest $\text{dS}/\text{dW}$, (2) strains at 30 and 40°C demonstrate similar behavior until 0.18 g/g-dried hcp, and (3) strains at 50 and 60°C show a similar behavior up to 0.17 g/g-dried hcp.

This suggests that the shrinkage strain in this RH region is dominated by the incremental water content, rather than the absolute water content. A portion of the evaporable water found at 5% RH at different temperature conditions may probably not contribute to the shrinkage strain. This can be explained by the hypothesis that the calcium-silicate-hydrate (C-S-H) meso-scale agglomeration as well as molecular-scale structures change at elevated temperatures, as suggested by Proton Nuclear Magnetic Resonance (1H-NMR) Relaxometry data (Wyrzykowski et al. 2017).

C-S-H is a highly basic solid-solution phase of widely varying composition, which is considered to be composed mainly of tobermorite-like anionic basal layers with associated calcium cations for charge balance (Richardson 2004, 2008; Richardson 2014). C-S-H is produced from solutions slightly supersaturated with portlandite during cement formation at a high pH level. It has an extremely disordered structure (Gartner 1997; Gartner et al. 2000) with many Ca–OH groups (Thomas et al. 2003), which could be partly alkylated to provide some Ca–OR groups. Recently, a new model for the structure of the wet C-S-H initially formed in Portland cement hydration was proposed by Gartner et al. (2017), which is referred to as the "GMC" model. In the GMC model, the freshly precipitated C-S-H is composed of tobermorite-like basal layers containing primarily dimeric silicate anions bonded to both sides of the basal CaO sheets, which are referred to as the mono C-S-H sheets herein. The negative charge of the mono C-S-H sheet repeating unit ($[\text{Ca}_2\text{Si}_2\text{O}_7]^{2-}$) is initially balanced by the fully hydrated divalent (Ca$^{2+}$) or univalent (CaOH$^+$) calcium cations, and each such cation is assumed to hold at least six oxygen atoms (likely more in the first stage of formation) in their inner coordination shell. Thus, fresh, wet C-S-H can be represented as a solid solution between the end members ($[\text{Ca}_2\text{Si}_2\text{O}_7]^{2-}$·$[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ = C$_3$S$_2$H$_6$) and ($[\text{Ca}_2\text{Si}_2\text{O}_7]^{2-}$·$2[\text{CaOH}(\text{H}_2\text{O})_5]^{2+}$ = C$_3$S$_2$H$_{11}$). If $\gamma$ represents the fraction of the low Ca/Si end members of this solid solution, it can readily be seen that, for $\gamma = 0.4$, the composition of the solid solution becomes C$_{1.7}$SH$_4$. This composition is the same as that assumed by Young and Hansen (1986) to account for the minimum amount of water required for complete cement hydration. The average distance of the C-S-H sheets, which is a function of how many water molecules hydrated the Ca ions on the C-S-H sheets, would be the key parameter for the shrinkage of the C-S-H sheet skeleton structure (Maruyama 2010, 2016). A portion of the interacting hydrated water molecules and Ca$^{2+}$ or Ca(OH)$^+$ ions on the surfaces of the C-S-H agglomeration might be easily released under drying/heating. In addition, temperature is expected to influence the equilibrium number of hydrated water molecules and the stability of the Ca ions on the C-S-H sheets. Consequently, the number of ion-hydrated water molecules on the surface of the C-S-H agglomeration, which has a reduced impact on the shrinkage of the C-S-H sheets structure skeleton, will decrease under heated and dried conditions.

Drying of the hcp induces microstructural reorganization (Tomes et al. 1957; Hunt et al. 1960; Parrott et al. 1980; Parrott and Young 1981; Litvan and Myers 1983; Völk et al. 1987; Maruyama et al. 2014), densification of the C-S-H, and the development of larger pores. Our measurements indicate that temperature also has a similar impact on the microstructure of hcp, which can be observed in the hcp cured at elevated temperatures during the hydration process (Giallucci et al. 2013; Bahafid et al. 2017, 2018). For the hcp shrinkage under the first
desorption, this microstructural reorganization, resulting from drying, is dominant compared to the reversible shrinkage (Helmuth and Turk 1967; Maruyama et al. 2014, 2015, 2016a, 2018a).

Figure 8 presents a schematic of the proposed mechanism for the change in hcp shrinkage behavior. At 20°C, the water almost comprises gel-pore water [(B) of Fig. 8] and interlayer water [(A) and (A') of Fig. 8], especially for less than 90% RH (Muller et al. 2013a). When the hcp is dried, the gel pore dries first (Muller et al. 2013b). Simultaneously, the C-S-H agglomerations and meso-scale texture change (Maruyama et al. 2014, 2015, 2017) and the irreversible shrinkage strain is produced (Maruyama 2016a, 2018a). Below 40% RH, the C-S-H molecule scale structure is stabilized and the shrinkage strain is dominated by the number of water molecules [(A') of Fig. 8] removed from the C-S-H structures. When the hcp is heated, the C-S-H meso-scale and atomic structures change and become dense due to the changes in the solubility equilibrium condition. These C-S-H meso-scale and molecular-scale alterations accompany loss of evaporable water at 5% RH [difference of (A) between 20°C and 60°C of Fig. 8]. Consequently, the larger gel-pore water [(C) of Fig. 8] is created from this densification at elevated temperature in a manner similar to an instantaneous reaction caused by a temperature change (Wyrzykowski et al. 2017). This occurred prior to the measurements taken in this study. Due to the creation of larger gel-pore water molecules [(C) of Fig. 8], which is easily evaporated in the higher RH range and will not create irreversible shrinkage during sample measurement, the tangent of $dS/dW$ (especially for 50°C and 60°C) decreases compared to that at 20°C. Furthermore, there is no inflection point at 0.08 g/g-dried hcp and a linear relation between $dS$ and $dW$ from 0.02 g/g-dried hcp to 0.17 g/g-dried hcp is observed for 50°C and 60°C (see Fig. 7).

This proposed hypothesis provides a reasonable explanation for the reduced drying shrinkage of the hcp at the elevated temperatures considered in this study as well as the opposite trends reported by Numao and Mishashi (1991).

5. Conclusion

Short-term length-change isotherms and desorption isotherms of matured hardened cement paste were measured at different temperature conditions, namely, 20, 30, 40, 50, and 60°C. For the short-term length-change isotherm, higher temperature conditions resulted in smaller drying shrinkage.

The observed relationship between incremental strain and incremental evaporable water content, for a selected starting RH of 5%, indicates that microstructural reorganization of C-S-H in the elevated temperature conditions accompanies the shrinkage. This, taken together with the difference in the sensitivity of the incremental strain to the incremental evaporable water content, suggests that the presence of evaporable water does not significantly contribute to the shrinkage of the hardened cement paste in higher temperature conditions.

It is suggested that the C-S-H meso-scale and atomic-scale alteration due to elevated temperatures create large gel-pore, which easily evaporates at high RH. During the pre-heating of the samples at the measuring temperature for one week, this C-S-H alteration and irreversible shrinkage should have occurred.

The study of C-S-H alteration under the wet/sealed and the elevated temperature conditions is remaining for future work.

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