Drying Shrinkage of Hardened Cement Paste and Its Relationship to the Microstructure

X. Wang, C. Wan, X. Zhang and H. Chen
College of Materials Science and Engineering, Chongqing University, China

ABSTRACT

The aim of the present study is to relate microstructure to the drying shrinkage of hardened cement paste. Three microstructural features, calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and pore structure were studied. A new method to determine the C-S-H content of hardened cement paste is presented. Drying shrinkage behavior of cement pastes were investigated by drying specimens through successive steps of RH 100% to 7% RH and re-saturating the specimens. The total shrinkage of cement paste after drying to 7% RH and irreversible shrinkage were decreased with the increasing amount of C-S-H and CH. Prolonged curing resulted in a paste with finer pore structure and more weight loss when dried in lower humidity. For a certain paste, the same amount of weight loss induced less liner shrinkage in the 54-23% RH range than in the 100-54% RH range. The total shrinkage of cement paste after drying to 7% RH and irreversible shrinkage decreases with increasing amount of C-S-H and CH. The formation of C-S-H increase the resistance of cement paste to shrinkage rather than enhance drying shrinkage by providing more gel pores and empty of which would bring large stress on the solid skeleton.

Keywords: hardened cement paste; drying shrinkage; calcium silicate hydrate; calcium hydroxide; pore structure

1.0 INTRODUCTION AND STRATEGY

Drying shrinkage is a characteristic property of hardened cement paste and also closely related with the durability of its corresponding concrete, for example, the drying shrinkage induced cracks can make concrete more permeable and easy to suffer chemical attack etc. Hardened cement paste is a highly porous material with a large specific surface area, primarily due to the porous microstructure of the main hydration product, CaO–SiO₂–H₂O (C-S-H) (Wittmann, 1973; Thomas, Jennings and Allen, 1999). Large quantities of water vapor are adsorbed on the internal surface of the hydration products (Setzer and Wittmann, 1974). The volume of hardened cement paste is sensitive to its moisture content (Juenger and Jennings, 2002). When exposed to environmental humidity, which is less than 100% RH, a saturated paste begins to lose water and shrink. The shrinkage on first drying is partly irreversible.

An approach towards a better understanding of the mechanism of drying shrinkage would be to study the relationship between microstructure even nanostructure and drying shrinkage of hardened cement paste. In the present study, the strategy was to vary the microstructure and relate the changes to the shrinkage behavior. Variation of the microstructure of cement paste was obtained by varying the curing time.

Calcium hydroxide (CH), C-S-H, and pore structure are chosen as the microstructural features for analysis in this study. Calcium hydroxide is believed to play a role in limiting the amount of shrinkage that occurs when a cement paste is dried (Mehta and Monteiro, 2006). Most of the shrinkage occurs in the C-S-H, the formation of C-S-H could increase drying shrinkage by increasing the level of deformation occurring within the paste, or reduce shrinkage by developing a rigid network of hydration product capable of resisting shrinkage. Furthermore, since drying process involves removal of water from pores which in turn creates substantial stresses and causes shrinkage (Hansen, 1987), the characterization of pore structure is important.

Solid state ²⁹Si MAS NMR, thermal analysis, MIP, and nitrogen sorption were used for microstructure analysis and the drying shrinkage of cement paste was determined from equilibrium drying experiments which was first proposed by Roper (Roper, 1965). Tests of drying shrinkage were generally conducted by directly subjecting samples to the ultimate RH. However, according to the classic experimental results of Roper, cement paste undergoes a series of different drying shrinkage mechanisms as the paste is equilibrated at successively lower relative humidity (Roper, 1965; Jennings, Thomas and Gevrenov, 2007). Thus, a more useful approach is to conduct stepwise drying, taking care to reach equilibrium at each RH level. Therefore, drying shrinkage could be studied in different RH ranges.
2.0 EXPERIMENTS

Cement pastes were prepared by hand mixing a ASTM Type I cement (Table 1) at W/C ratio of 0.4 with de-ionized water for 5 minutes. Samples were cast in polystyrene vials (27 mm diameter, 50 mm height) and sealed in air-tight containers in a 24 °C water bath. After the first 24 h, samples were demoulded and cured at room temperature (24 ± 3 °C) in an air-tight container filled with lime-saturated water for ages of 7, 28, 56 and 180 days. After the specified curing time, samples were removed from the lime water and prepared for tests.

Table 1. Chemical analysis of ASTM Type I Portland cement

<table>
<thead>
<tr>
<th>Mineral composition</th>
<th>Weight percent (%)</th>
<th>Chemical Composition</th>
<th>Weight percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>48.26</td>
<td>SiO2</td>
<td>21.84</td>
</tr>
<tr>
<td>C3S</td>
<td>26.23</td>
<td>Al2O3</td>
<td>4.96</td>
</tr>
<tr>
<td>C3A</td>
<td>7.21</td>
<td>CaO</td>
<td>64.97</td>
</tr>
<tr>
<td>C4AF</td>
<td>10.64</td>
<td>Fe2O3</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MgO</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO3</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Loss of ignition (%)</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The equilibrium drying experiments were conducted after the method proposed by Roper (Roper, 1965) and Jennings (Jennings, Thomas and Gevrenov, 2007). Thin (0.80mm) discs were sliced using a water-lubricated diamond precision saw. Initially saturated discs were progressively dried step-by-step via enclosing them over saturated salt solutions with different equilibrium relative humidity in sealed desiccators. The desiccators were filled with nitrogen gas to prevent carbonation. The successive steps of drying were heated to 1000 °C at 20°C/min, under a constant flow of nitrogen.

3.0 DETERMINATION OF C-S-H CONTENT

In the present study, the C-S-H content was determined from a combination of thermogravimetric analysis and single pulse 29Si solid state MAS NMR. The strategy was to calculate the percentage of SiO2 reacted in the raw materials via 29Si NMR analysis.

Single pulse 29Si solid state MAS NMR spectra were acquired using a Bruker AVANCE III 400MHz spectrometer (operating frequency of 79.49 MHz for 29Si). Samples were packed into 7 mm ZrO2 rotors and spun at 6 kHz. The spectra were acquired over 10000 scans using a pulse recycle delay of 3 s, a pulse width 4.5 μs, and an acquisition time 10.29 ms.

Deconvolution of the spectra provides quantitative information on the fractions of Si present in different tetrahedral environments, Qn, where n denotes the connectivity of the silicate tetrahedron: thus Q0 represents isolated tetrahedra in the anhydrous paste (at around -71 ppm); Q1 represents chain-end group tetrahedral (at round -79 ppm), Q2 represents middle groups where both adjacent tetrahedral are occupied by silicon tetrahedral (at round -83 ppm), Q3 represents branching sites and Q4 cross-linking sites in a three dimensional framework (Cong and Kirkpatrick, 1996; Love, Richardson and Brough, 2007; Girão, Richardson and Porteneuve, 2007; He and Hu, 2007). Thus α = I(Q0 +Q1+Q2+Q3+Q4) / I(Q0 +Q1+Q2+Q3+Q4), where α denotes the percentage of Si reacted. The percentage of SiO2 reacted equals the percentage of Si reacted.

In thermogravimetric analysis, the weight of hydrated cement paste after firing to 1000 °C, W1000, represents the weight of the raw cement used. Thus, W(SiO2) =0.2184*W1000, where W(SiO2) denotes the weight of SiO2 (SiO2 makes up 21.84% of the original cement as shown in Table 1). And Wr(SiO2) =α*W(SiO2), where Wr(SiO2) denotes the weight of SiO2 reacted.

The stoichiometry of C-S-H is assumed to be C3.4S2H3 (Mindess and Young, 1981; Olson and Jennings, 2001). According to the law of conservation of mass, that is, the quantity of the SiO2 reacted equals to that of the SiO2 in the hydration products, W(C-S-H) * M(S2) / M(C3.4S2H3)= Wr(SiO2), where M denotes molar mass, M(S2) / M(C3.4S2H3) denotes the SiO2 content in C3.4S2H3, M(S2) / M(C3.4S2H3)=0.3293. Thus, W(C-S-H) = Wr(SiO2) * M(C3.4S2H3) / M(S2)=0.6632*α*W1000, where W(C-S-H) denotes the weight of C-S-H. Therefore, the C-S-H content can be calculated.
using the equation: \( \%C-S-H = \frac{W(C-S-H)}{W_{\text{paste}}} = 0.6632a\times W_{1000}/W_{\text{paste}} \), where \( W_{\text{paste}} \) denotes the weight of dried paste at 105 \(^{\circ}\)C.

## 4.0 RESULTS AND DISCUSSION

### 4.1. Characterization of Microstructure

**CH and C-S-H**

Typical TG-DSC results were presented in Fig. 1, and corresponds to the results obtained for cement paste hydrated for 28 days. The first endothermic peak of DSC curve is attributed to the dehydroxylation of C-S-H phase, corresponding to the mass loss on the TG profile around 200 \(^{\circ}\)C (Neto, Cincotto and Repette, 2008; Alarcon-Ruiza, Platret, Massieu and Ehrlacher, 2005; Esteves, 2011). The second major peak of DSC curve is also endothermic and mainly corresponds to the decomposition of calcium hydroxide between 400-500 \(^{\circ}\)C or so (Neto, Cincotto and Repette, 2008; Alarcon-Ruiza, Platret, Massieu and Ehrlacher, 2005; Esteves, 2011), the exact temperature interval can be clearly identified by DSC curve as shown in Fig. 1. No representative peak was found at DSC curve around 800 \(^{\circ}\)C. The quantity of calcium hydroxide in the pastes determined from the thermogravimetric curves are given in Table 2 (as percentage of paste dried at 105 \(^{\circ}\)C). As expected, calcium hydroxide contents of samples increase with the curing time.

Typical single-pulse \(^{29}\)Si solid state NMR results were presented in Fig. 2, and corresponds to the results obtained for cement paste hydrated for 28 days, the same as in Fig. 1. In the studied system, no Q\(_3\) and Q\(_4\) were found. The results of the deconvolution of spectra are given in Table 2. As shown, C-S-H contents of cement pastes and Q\(_2\) contents of C-S-H increase with the curing time.

**Pore structure of C-S-H**

In this study, nitrogen adsorption gives information about pores in the diameter range of 1.7-50 nm, which include small capillaries and gel pores that are associated with the C-S-H product (Mehta and Monteiro, 2006; Taylor, 1997).

![Fig. 1. Thermal analysis data for the 28-day-old cement paste](image1)

![Fig. 2. Single-pulse\(^{29}\)Si solid state NMR spectra for the 28-day-old cement paste](image2)

As shown in Fig. 4, pores in this range are generally characterized by two classes: pores located around 30 nm and around a few nanometers, respectively. Pore size distribution for cement pastes with different curing times are displayed in Fig. 5, and the evolution of average pore diameter with curing time is shown in Fig. 6. Generally, prolonged curing increased the volume of pores around a few nanometers and resulted in a finer pore structure.

### Table 2. Results from thermal analysis, \(^{29}\)Si NMR spectra and calculation described in section 3.

<table>
<thead>
<tr>
<th>Age</th>
<th>%CH</th>
<th>%Q(_0)</th>
<th>%Q(_1)</th>
<th>%Q(_2)</th>
<th>%SiO(_2) reacted</th>
<th>W(_{1000})</th>
<th>W(_{\text{paste}})</th>
<th>%C-S-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 days</td>
<td>15.43</td>
<td>38.36</td>
<td>58.38</td>
<td>3.36</td>
<td>61.64</td>
<td>8.7390</td>
<td>10.1585</td>
<td>35.17</td>
</tr>
<tr>
<td>28 days</td>
<td>17.70</td>
<td>28.30</td>
<td>65.35</td>
<td>6.35</td>
<td>71.70</td>
<td>9.0855</td>
<td>10.6988</td>
<td>40.38</td>
</tr>
<tr>
<td>56 days</td>
<td>17.86</td>
<td>24.36</td>
<td>63.17</td>
<td>12.48</td>
<td>75.65</td>
<td>8.5651</td>
<td>10.2888</td>
<td>41.74</td>
</tr>
<tr>
<td>180 days</td>
<td>20.58</td>
<td>8.24</td>
<td>68.17</td>
<td>23.59</td>
<td>91.76</td>
<td>8.3601</td>
<td>10.4880</td>
<td>48.51</td>
</tr>
</tbody>
</table>

\( %\text{CH} = \) calcium hydroxide as % of paste weight dried at 105 \(^{\circ}\)C. \( %\text{C-S-H} = \) calcium silicate hydrate as % of paste weight dried at 105 \(^{\circ}\)C.
The curves shown in Figs. 7a and 7b illustrate drying shrinkage and weight loss versus time during the equilibrium drying and re-saturating process. The data shown are for the 28-day-old cement paste.

4.3. Relationship Between Drying Shrinkage and Microstructure

Shrinkage resisting phase and drying shrinkage In the 100 - 54% RH range, shrinkage at an earlier age (7 days) is relatively large, but at later ages, these values are lower. It is suggested that the main driving force of shrinkage in this range is associated with capillary tension (Taylor, 1997). On the one hand, according to the weight loss data in Table 3, less volume of pores is dried to empty with age which means fewer menisci was formed, with less water having high capillary tension, resulting in lower stress and subsequently lower shrinkage strains. On the other hand, as indicated by the $^{29}$Si NMR spectra data, extended curing not only increased the C-S-H content in hydrated cement paste but also increased the polymerization of C-S-H according to the $\% Q_2$.
Fig. 7. (a) drying shrinkage of the 28-day-old hardened cement paste under equilibrium drying and re-saturating, (b) weight loss of the 28-day-old hardened cement paste under equilibrium drying and re-saturating

Table 3. Drying shrinkage and weight loss results for cement pastes of different curing time

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage (% in length change)</th>
<th>Weight loss (% in mass change)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>100-54% RH</td>
</tr>
<tr>
<td>7 days</td>
<td>0.566/13.17</td>
<td>0.359/8.52</td>
</tr>
<tr>
<td>28 days</td>
<td>0.536/10.87</td>
<td>0.292/5.60</td>
</tr>
<tr>
<td>56 days</td>
<td>0.509/11.98</td>
<td>0.266/5.49</td>
</tr>
<tr>
<td>180 days</td>
<td>0.459/11.84</td>
<td>0.264/5.44</td>
</tr>
</tbody>
</table>

Irreversible weight loss was not calculated because weight loss can be almost fully regained.

In the 54 - 23% RH range, shrinkage is likely due to the empty of smaller pores (e.g., < 10 nm), which are associated with the main hydration product, i.e., C-S-H. The volume of smaller pores increases over time as indicated by the %CH data in Table 2. Thus, the resulting cement paste is stiffer and possesses a higher modulus, which would shrink less even under the same stress.

In the 23 - 7% RH range, weight loss and shrinkage show very relatively tiny decrease trend with curing time. Shrinkage in this range are likely due to the empty of the smallest pores which cannot be detected by the nitrogen porosity analysis (Mindess and Young, 1981; Juenger and Jennings, 2001).

On the whole, in the 100 - 7% RH range, the total and irreversible shrinkage decrease with curing time, that is, with the increasing content of C-S-H and CH.

From the shrinkage analysis above, it could be concluded that CH and C-S-H appears to increase the resistance of hydrated cement paste to drying shrinkage and that the shrinkage of cement paste depends mainly on its resistance to deformation.
Table 4. Ratio of weight loss and relationship between weight loss and shrinkage in each RH range

<table>
<thead>
<tr>
<th>Curing time</th>
<th>100-54% RH</th>
<th>54-23% RH</th>
<th>23-7% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 days</td>
<td>64.69/0.0421</td>
<td>22.86/0.0399</td>
<td>12.45/0.0530</td>
</tr>
<tr>
<td>28 days</td>
<td>51.52/0.0523</td>
<td>33.11/0.0475</td>
<td>15.36/0.0437</td>
</tr>
<tr>
<td>56 days</td>
<td>45.82/0.0484</td>
<td>41.65/0.0322</td>
<td>12.52/0.0567</td>
</tr>
<tr>
<td>180 days</td>
<td>46.02/0.0485</td>
<td>43.06/0.0240</td>
<td>10.91/0.0566</td>
</tr>
</tbody>
</table>

Pore structure and drying shrinkage

Table 4 summarizes the ratio of weight loss occurred in each RH range for pastes with different curing time. For the 7-day-old paste, 64.69% of the weight loss occurred in the 100 - 54% RH range. For older pastes, the ratio of weight loss in this range decreases and more ratio of weight loss occurred below 54% RH. Data from nitrogen sorption as indicated in Fig. 4 and 6 shows that older pastes have a finer pore structure.

For the 7-day-old paste, 1% of weight loss induces 0.0421% of linear shrinkage in the 100 – 54% RH range. In the 54 – 23% RH range, 1% of weight loss induces only 0.0399% of linear shrinkage. Detailed results for pastes of different curing time are summarized in Table 4. It could be identified that for a certain paste, the same amount of weight loss induced less linear shrinkage in the 54 - 23% RH range than in the 100 - 54% RH range. A reasonable explanation could be that the modulus of cement paste increases after drying, and thus will shrink less even under higher stress. There is evidence in literature that drying caused an increase in polymerization (Bentur, Berger, Lawrence Jr., Milestone, Mindess and Young, 1979), which would result in a stiffer paste. Besides, the mechanical behaviour of cement paste could be described in the framework of porous media, and the bulk modulus of paste would increase with the loss of water (Ghabezloo, Sulem, Guédon, Martineau and Saint-Marc, 2008; Vlahinić, Jennings and Thomas, 2009).

5.0 CONCLUSIONS

C-S-H grows more and stronger over time, resulting in a stiffer and denser paste structure. The total shrinkage of cement paste after drying to 7% RH and irreversible shrinkage decreases with increasing amount of C-S-H and CH. The formation of C-S-H increase the resistance of cement paste to shrinkage rather than enhance drying shrinkage by providing more gel pores and empty of which would bring large stress on the solid skeleton. Detailed study of drying shrinkage and weight loss of cement pastes in different RH ranges indicates that prolonged curing time resulted in a paste with a finer pore structure and more weight loss when dried in lower humidity and that for a certain paste, the same amount of weight loss induced less linear shrinkage in the 54 - 23% RH range than in the 100-54% RH range. This would probably be a reason why the presence of more gel pores doesn’t bring larger drying shrinkage.

Acknowledgement

We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China, Grant No. 51172292, named as Insight into the Micro- and Nano- Scale Mechanism of Drying Shrinkage of Hardened Cement Paste.

References


