Cement reaction and resultant physical properties of cement paste
Ippei Maruyama, Go Igarashi

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1. Introduction

A discussion of the structural performance of reinforced concrete structures and its time dependence requires consideration of the time dependence of the properties of concrete, taking into account the concreting and curing processes, with the hydration of cement from the time of water supply as the starting point (Sato et al. 2008).

Cement hydration kinetics models have been proposed for a long time (Taplin 1959; Kondo and Ueda 1968; Tomosawa 1974; Jennings and Johnson 1986), and in recent years many studies have been proposed as the scale and speed of numerical calculations have increased (Thomas et al. 2011). For the phase composition resulting from the hydration reaction, an experiment-based hydration reaction formula was proposed quite some time ago (Osbaeck 1992), and more recently, the development of data for thermodynamic equilibrium calculations has been progressing, leading to the proposal of simple and relatively high-accuracy empirical formulas. Further, background information about raising the correlation of these empirical formulas was also discussed.

Further, background information about raising the correlation of these empirical formulas was also discussed.

Extensive research has been conducted by Powers and Brownyard in terms of the microstructure and properties of cement paste (Powers and Brownyard 1947; Powers 1958). A gel-space ratio theory allowing quantitative prediction of the compressive strength of mortar from the microstructure has been proposed (Powers 1958). Based on the study of water vapor adsorption behavior, a high correlation between the water vapor adsorption BET specific surface area and chemically bound water has been pointed out (Powers 1946).

Subsequently, as various numerical models were proposed reflecting the increasing availability of numerical calculation power, experimental studies to associate physical properties and hydrated (cured) cement information have been conducted (Powers and Brownyard 1947; Osbaeck 1992, Bouniz 1996; Haecker 2005).

As analytical techniques have improved and thermodynamic equilibrium calculation databases are now available in the field of cement chemistry, further development of fundamental data for the quantitative evaluation of the physical properties of hardened cement paste generated as the result of hydration is essential from the perspective of concrete engineering.

From this perspective, this study consolidates data about the hydration reaction and resultant physical properties, using two different water-cement ratios and three different Portland cement pastes. Further, it selects among the indices indicating the microstructure of cement paste those with the highest correlation and proposes engineering formulas for predicting physical properties.
It is noteworthy that there are companion papers showing the physical data of cement paste made with the same Portland cement. Drying shrinkage (Maruyama 2010) as well as the development of autogenous shrinkage and linear expansion coefficient (Maruyama et al. 2013) for the cements used in this study have been reported elsewhere. The results for ordinary Portland cement subjected to initial high temperature curing and which were subjected to further hydration reaction analysis. The influences such as N55, indicating the binder type and the water-binder ratio. The OM30-SA omni mixer (Chiyoda Machinery, 30 liter capacity, hydraulic motor drive) was used for mixing. After three minutes mixing followed by scraping, mixing was done for an additional three minutes. The mixing volume was 25 L. After remixing for 4 to 6 hours until bleeding stopped, the cement was poured in disposable trays made of polypropylene and measuring 100 × 150 × 20 mm. Immediately after pouring, the specimens were sealed by wrapping them in plastic film made of polyvinylidene chloride (PVC), then covering them with adhesive aluminum tape, and further sealing them in a zippered aluminum bag.

All the samples were allowed to stand in a 20±1°C constant temperature chamber.

### 2.2 Cement hydration evaluation

Samples whose hydration was stopped at the designated ages (0.5, 0.75, 1, 3, 7, 14, 28, 91, 182, and 364 days) were used. The samples of each material age were crushed into pieces of 20 mm or less with a hammer, and then finely ground using a high speed vibrating sample crusher. The milled sample powder was immediately immersed for about 30 minutes in acetone, after which the cement sample was then again immersed in acetone for an additional six hours, after which the acetone was again separated. After the hydration reaction was stopped by acetone, the samples were dried for two weeks in a desiccator using circulated air scrubbed using carbon dioxide absorbent and a saturated lithium chloride aqueous solution at the constant temperature of 20°C. After drying, the samples were graded with a 150 μm sieve, and only the powder under the sieve was used for the various measurements.

Measurement of powder X-ray diffraction was conducted using a D8 ADVANCE X-ray diffractometer (Bruker AXS) under the following conditions: Cu-Kα X-ray source, 40 kV tube voltage, 40 mA tube current, 2θ=5–65° scanning range, 0.02° step width, and 0.5°/min scanning speed. The samples used for measurement consisted of powder samples whose hydration was stopped and which underwent humidity conditioning to which corundum (α-Al2O3) was admixed at the rate of 10 wt% in terms of inner percentage as an internal standard. Rietveld analysis was done for the entire chart.

<table>
<thead>
<tr>
<th>Type</th>
<th>Density (g/cm³)</th>
<th>Blaine value (cm²/g)</th>
<th>LOI</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Cl⁻</th>
<th>Total</th>
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<tr>
<td>Ordinary Portland cement (N)</td>
<td>3.16</td>
<td>3110</td>
<td>0.64</td>
<td>21.8</td>
<td>4.49</td>
<td>2.90</td>
<td>63.9</td>
<td>1.84</td>
<td>2.26</td>
<td>0.20</td>
<td>0.38</td>
<td>0.007</td>
<td>98.4</td>
</tr>
<tr>
<td>Moderate heat Portland cement (M)</td>
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<td>3210</td>
<td>0.80</td>
<td>23.3</td>
<td>8.80</td>
<td>3.90</td>
<td>63.3</td>
<td>0.90</td>
<td>2.40</td>
<td>0.30</td>
<td>0.35</td>
<td>0.000</td>
<td>99.1</td>
</tr>
<tr>
<td>Low heat Portland cement (L)</td>
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<td>3400</td>
<td>0.70</td>
<td>26.3</td>
<td>3.80</td>
<td>3.20</td>
<td>62.9</td>
<td>0.70</td>
<td>2.40</td>
<td>0.15</td>
<td>0.41</td>
<td>0.005</td>
<td>99.6</td>
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<table>
<thead>
<tr>
<th>Type</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>M</th>
<th>C₆H₆</th>
<th>C₆H₄</th>
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</thead>
<tbody>
<tr>
<td>N</td>
<td>62.2±1.0</td>
<td>18.3±0.8</td>
<td>5.6±0.5</td>
<td>9.8±0.9</td>
<td>1.3±0.2</td>
<td>1.2±0.2</td>
<td>1.5±0.1</td>
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<tr>
<td>M</td>
<td>41.6±1.0</td>
<td>38.6±1.4</td>
<td>3.7±0.3</td>
<td>12.7±0.3</td>
<td>0.8±0.2</td>
<td>2.4±0.3</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>L</td>
<td>24.5±0.6</td>
<td>61.3±1.6</td>
<td>2.2±0.3</td>
<td>8.3±0.3</td>
<td>0.7±0.2</td>
<td>2.4±0.3</td>
<td>0.6±0.1</td>
</tr>
</tbody>
</table>

where C:CaO, S:SiO₂, A:Al₂O₃, F:Fe₂O₃, M:MgO, s:SO₃, H₂O.
obtained using the TOPAS ver. 4.2 software (Bruker AXS). Alite (C₃S), belite (C₂S), aluminate phase (C₃A), ferrite phase (C₄AF), periclase (MgO (M)), lime (Free-CaO), calcite (CaCO₃ (Cc)), gypsum (CaSO₄ · 2H₂O (C₅H₂)), bassanite (CaSO₄ · 0.5H₂O (C₅H₀.₅)), portlandite (Ca(OH)₂ (CH)), ettringite (C₃A · 3CaSO₄ · 32H₂O (Ett)), monosulfate (C₃A · CaSO₄ · 12H₂O (Ms)), and hydrogarnet (C₃AH₆ (Hg)), as minerals and cement hydration products, and α-Al₂O₃ (10wt%) admixed to the analysis sample as the internal standard, were chosen to be quantified. As the parameters related to the crystal structure of the C₃S, C₂S, C₃A, and C₄AF crystalline phases of the minerals for quantification, those in the ICSD Database (ICSD 2006) were used. The mass of amorphous materials was calculated according to Equation (1) based on the quantitative value of internal standard α-Al₂O₃ (Bish and Howard 1988).

\[ A = \frac{(100 \times S_R - S)}{S_R \times (100 - S)/100} \]  

where \( A \) = amorphous material mass, \( S \) = mixing ratio (%) of α-Al₂O₃, and \( S_R \) = quantitative value (%) of α-Al₂O₃. The maximum error in XRD/Rietveld analysis was calculated from the analytical error in pattern fitting of Rietveld analysis and the measurement error of the quantitative values obtained from three measurements. The standard deviation of quantitative values for the cement materials in unhydrated cement was ±1.0 mass% for C₃S, ±1.6 mass% for C₂S, ±0.5 mass% for C₃A, and ±0.9 mass% for C₄AF.

In assessing the reaction rates of the minerals in the various cements and the phase composition including the solid phase as affected by humidity conditioning, the H₂O/CaO ratio under different drying states was considered, and the hydration rate was assessed by converting all components into anhydrous matter by using the chemical composition shown in Table 3 and the chemically bound water values. Here, the humidity after

<table>
<thead>
<tr>
<th>Hydrates</th>
<th>Drying state</th>
<th>H/C</th>
<th>Composition formula</th>
<th>Molar mass (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H</td>
<td>1000°C</td>
<td>0</td>
<td>C₅H₆</td>
<td>155</td>
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<tr>
<td></td>
<td>105°C</td>
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<td>C₅H₁₅</td>
<td>182</td>
<td>2.60</td>
<td>2)</td>
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<td></td>
<td>11%RH,20°C</td>
<td>1.47</td>
<td>C₅H₁₅</td>
<td>193</td>
<td>2.41</td>
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<td></td>
<td>Saturated</td>
<td>1.47</td>
<td>C₅H₁₅</td>
<td>193</td>
<td>2.41</td>
<td>4)</td>
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<tr>
<td>Ett</td>
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<td>C₅A·3(CS)·H₆</td>
<td>679</td>
<td>—</td>
<td></td>
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<tr>
<td></td>
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<td>2.00</td>
<td>C₅A·3(CS)·H₁₂</td>
<td>895</td>
<td>2.38</td>
<td>5)</td>
</tr>
<tr>
<td></td>
<td>11%RH,20°C</td>
<td>5.33</td>
<td>C₅A·3(CS)·H₃₂</td>
<td>1255</td>
<td>1.78</td>
<td>6)</td>
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<tr>
<td></td>
<td>Saturated</td>
<td>5.33</td>
<td>C₅A·3(CS)·H₃₂</td>
<td>1255</td>
<td>1.78</td>
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<tr>
<td>Ms</td>
<td>1000°C</td>
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<td>623</td>
<td>1.99</td>
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<tr>
<td></td>
<td>Saturated</td>
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<td>623</td>
<td>1.99</td>
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<td>105°C</td>
<td>0.88</td>
<td>C₅A·H₆</td>
<td>378</td>
<td>2.52</td>
<td>7)</td>
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<tr>
<td></td>
<td>11%RH,20°C</td>
<td>0.88</td>
<td>C₅A·H₆</td>
<td>378</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saturated</td>
<td>0.88</td>
<td>C₅A·H₆</td>
<td>378</td>
<td>2.52</td>
<td>8)</td>
</tr>
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<td>C-A-H</td>
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<td>C₅A·H₆</td>
<td>326</td>
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<tr>
<td></td>
<td>105°C</td>
<td>1.75</td>
<td>C₅A·H₆</td>
<td>452</td>
<td>2.52</td>
<td>7)</td>
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<tr>
<td></td>
<td>11%RH,20°C</td>
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<td>C₅A·H₁₃</td>
<td>561</td>
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<tr>
<td></td>
<td>Saturated</td>
<td>3.25</td>
<td>C₅A·H₁₃</td>
<td>561</td>
<td>2.05</td>
<td>8)</td>
</tr>
<tr>
<td>C-F-H</td>
<td>1000°C</td>
<td>0</td>
<td>C₅F·H₆</td>
<td>384</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>105°C</td>
<td>1.75</td>
<td>C₅F·H₆</td>
<td>510</td>
<td>2.84</td>
<td>9)</td>
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<tr>
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<td>11%RH,20°C</td>
<td>3.25</td>
<td>C₅F·H₁₃</td>
<td>618</td>
<td>2.16</td>
<td>10)</td>
</tr>
<tr>
<td></td>
<td>Saturated</td>
<td>3.25</td>
<td>C₅F·H₁₃</td>
<td>618</td>
<td>2.16</td>
<td>8, 10</td>
</tr>
</tbody>
</table>

1) The molecular weight of C-S-H when x is assumed to be 1.7 is listed.
2) References : Jennings (2000), Taylor (1986)
4) In the present study, the adsorbed water at the condition above 11% RH is assumed to behaves like a bulk water.
6) References : Tennis and Jennings (2000), Poellmann et al. (1993)
8) This has been reported to become C₅A·H₆ at relative humidity of 88% or higher, but it was decided to consider it to be stable C₅A·H₆ as a crystal in consideration of the easy dehydration condition.
9) Because of missing data, the density was calculated by assuming the same crystal structure as C₅A·H₆.
10) It is generally accepted that Fe forms a liquid solution partly substituting with Al in C-A-H, while they are separated for convenience in this study.
humidity conditioning is assumed to be 11%RH. Further, in this study, in view of the changes in the Ca/Si atomic ratio due to the hydration reaction, we identified the phase composition through the following iterative calculation process from the values obtained by Rietveld analysis.

1. Each phase in cement paste is converted into anhydride. Then, the C-S-H amount value is assigned by using a temporary Ca/Si atomic ratio of C-S-H, such as 1.7.

2. The hydration reaction rate of each anhydrous phase is calculated.

3. The amounts of Al₂O₃ and Fe₂O₃ in unhydrated cement minerals and crystalline hydrates are calculated based on the Rietveld analysis results. The difference in the amounts of Al₂O₃ and Fe₂O₃ between cement minerals and hydrates is considered to have been used in the formation of C-A-H or C-F-H in amorphous material (Collepardi et al. 1978).

4. The amounts of CaO and SiO₂ in unhydrated cement minerals, crystalline hydrates, and C-A-H and C-F-H are calculated based on the Rietveld analysis results and the results of step 3) above. The difference in the amount of CaO and SiO₂ between the hydrated cement minerals and hydrates C-A-H and C-F-H are considered to have been used in the formation of C-S-H.

5. The Ca/Si atomic ratio of C-S-H is calculated and all amorphous material is converted into anhydride.

6. The phase composition can be identified as the value at convergence through repetition of the above calculations.

Through the iterative calculation of 1) through 6), convergence of the Ca/Si atomic ratio of C-S-H is achieved and the calculation is completed. It should be noted that in the scope of this study, differences in molecular weight due to differences in the Ca/Si atomic ratio of C-S-H were taken into account, but owing to the limited amount of data available, it was assumed that there are no changes in the H/Si ratio and density of C-S-H.

Figure 1 shows an overview of the above-described iteration algorithm. The amount of matter of each phase is identified through that calculation flow. Furthermore, the phase composition in terms of equivalent volume was obtained by using the amount of chemically bound water and density of each hydration product in the sealed state described in Table 3.

In this study, we measured the ignition loss for samples after humidity conditioning, for the purpose of verifying the XRD/Rietveld method and examining the possibility of developing a physical property assessment index system. Measurements were performed using a TG-DTA 2010 SA (Bruker AXS). Samples of mass 20±2 mg were subjected to thermogravimetric (TG) analysis in the temperature range from room temperature to 1000°C with a rate of temperature increase of 10 °C/min under an N₂ flow. The amount of chemically bound water was calculated from ignition loss.

2.3 Compression loading test

The compressive strength and Young's modulus were measured using φ50 × 100 mm specimens fabricated from cement paste at the ages of 1, 3, 7, 14, 28, 91, 182, and 364 days. The sealed samples were demolded immediately prior to testing, and their loading face was polished. The tests were conducted on three specimens and the results were averaged. Young's modulus was determined by measuring vertical strain with a com-
pressometer (50 mm rating interval, 1/1000 mm accuracy) at the lording one-third of the maximum, and then using least squares approximation to calculate Young's modulus as the ratio of compressive stress to vertical strain. Because the compressive strength results varied widely from the age of 91 days for L40 and M40, and at the age of 364 days for L55 and M55, compressive strength was not evaluated.

2.4 Ultrasonic wave velocity test
Prismatic specimens of 40 × 40 × 160 mm made of cement paste were demolded at the age of 0.5 days, the ultrasonic wave arrival time was measured at the ages of 0.5, 0.75, 1, 1.5, 2, 3, 5, 7, 14, 28, 91, and 182 days, and Poisson's ratio was calculated as an average of the values obtained for three specimens. After demolding, the specimens were sealed at all times with aluminum adhesive tape except at the measurement points, and the measurement points were also sealed when measurement were not being performed to prevent as much as possible the escape of moisture.

Measurement of the ultrasonic wave arrival time was done using Panametrics-NDT™ ultrasonic transducers (V103-RM, V153-RM), Panametrics-NDT™ pulser-receiver 5077PR (Olympus), and digital scope oscilloscope TDS2012B (Tektronix). Using pulsed voltage of -400 V, probe frequency of 1.0 MHz, and pulse repetition frequency (PRF) of 100 Hz as the measurement conditions, the longitudinal wave arrival time and transverse wave arrival time were respectively measured at the middle of each specimen by the transmission method from the difference between the reference waveform and the transmitted waveform. The results were converted into longitudinal wave propagation speed and transverse wave propagation speed. Determination of the arrival time was done at the maximum peak waveform by using the time showing the maximum value. The thickness of the specimen s used for this calculation was 40 mm throughout.

Poisson's ratio was calculated from these data with Equation (2), based on elastic theory, using the speed ratio of the longitudinal and transverse waves.

\[
\nu = \frac{1 - 2\left(\frac{V_T}{V_L}\right)^2}{2 - 2\left(\frac{V_T}{V_L}\right)^2}
\]  
(2)

where \(\nu\) = Poisson's ratio (−), \(V_L\) = Longitudinal wave propagation speed (km/s), \(V_T\) = transverse wave propagation speed (km/s).

Further, from Poisson's ratio and the apparent density, Young's modulus (longitudinal elastic modulus) is obtained by Equation (3).

\[
E = \frac{(1+\nu)(1-2\nu)\nu}{1-\nu}\rho = 2(1+\nu)\nu\rho
\]  
(3)

where \(\rho\) = apparent density (g/cm³), \(E\) = Young's modulus (GPa), \(G\) = shear modulus (GPa), and \(K\) = bulk modulus (GPa).

Because no change in mass should occur in a sealed condition, the apparent density of the hardened cement paste was assumed to be a constant value from immediately after water supply, and was calculated from the cement density indicated in Table 1 and the water-cement ratio.

Equations (2) and (3) are based on the elasticity theory. Data supporting their applicability to hardened cement paste at an early material age when plastic deformation due to fine cracks is most likely to occur is limited. However, given the experimental confirmation of the tendency of a value with no volume change such as water (\(\nu = 0.5\)) to change over time to a value that converges closely toward Poisson's ratio for concrete, which is generally known, as the result of curing, as predicted and confirmed by previous studies (Kawasumi 1994; Abeele et al. 2009), these equations were judged capable of yielding the elastic Poisson's ratio of hardened cement paste.

2.5 Water vapor adsorption test
Water vapor adsorption tests were carried out on samples graded between 25 μm and 75 μm after humidity conditioning. A Hydrosorb 1000 (Quantachrome) was used for measurement based on the volume method. As a pre-processing condition for the samples, the samples were heated for one hour at 105 °C using a mantle heater under the condition of vacuum degassing by a rotary pump (ultimate pressure performance: 6.7 × 10⁻² Pa). During measurement, a sample cell was placed in a controlled temperature environment of 20±0.1 °C using constant temperature water tank control. Allowable pressure differential of 0.05 mmHg and equilibrium time of 120 s were adopted for measurement, and in terms of measurement points, 5% increments from 5% RH to 95% RH were used, with 98%RH as the final point. Based on the results of the water vapor adsorption test, we calculated the BET specific surface area using the data in the region of 5%RH to 30%RH. At that time, we used the value of 0.114 nm² as the area occupied by one water molecule (Mikhail and Selim 1966).

2.6 Thermal conductivity measuring device
A Kemtherm QTM-D3 (Kyoto Electronics Manufacturing), a box-type probe meter using the transient hot wire method was used for measurement. Thermal conductivity was obtained by Equation (4).

\[
\lambda = K \cdot I \cdot \ln\frac{T_2/T_1}{V_2-V_1} - H
\]  
(4)

where \(\lambda\) = thermal conductivity of the hardened cement paste (W/(m·K)), \(K\), \(H\) = constants determined by the probe, \(V_1, V_2\) = electromotive force of the thermocouples at times \(T_1\) and \(T_2\), respectively (mV), and \(I\) = current flowing through the heating wire (A). In this experiment,
I = 2.00 A, and the measurement time is 60 s.

The specimens described in section 2.1 were removed from their tray at the time of measurement, covered with a PVC film, turned upside down to make their bottom side face up, and fitted with the probe used for measurement. The film served to control moisture escape caused by heating during measurement, and the fact that it did not affect measurements was confirmed during preliminary tests. The materials ages were 0.5, 0.75, 1, 1.5, 2, 3, 5, 7, 14, 21, 28, 91, and 182 days, and the measurement value was the average for five specimens.

3. Experimental results and discussion

3.1 Hydration analysis
Figure 2 shows the relationship between the hydration reaction rate of the cement minerals and the material age of each cement paste. The error bars represent 1 standard deviation of variability during measurement and analytical error during Rietveld analysis. Figure 3 shows the development of phase composition, calculated from the composition of the unhydrated cement, the reaction rate in Fig. 2, and the analysis flow shown in Fig. 1. In order to verify the validity of this development, the comparison of chemically bound water measured by TG and the chemically bound water calculated from the phase composition is shown in Fig. 4. As shown in this figure, there is a good correlation between the two, thus conferring a certain degree of validity to the calculated phase compositions.

3.2 Strength, Young's modulus, and Poisson’s ratio
Figures 5 to 8 show the development in compressive strength (compression test), Young's modulus (compression test), Young's modulus (ultrasonic test), and Poisson's ratio (ultrasonic test), respectively.

As shown in Fig. 5, development of compressive strength shows sign of almost completely leveling off at the age of 1 year for N55. M and L show slow strength development, reflecting the hydration rate. Figures 6
Fig. 5 Development of compressive strength of cement pastes.

Fig. 6 Development of Young’s modulus of cement pastes measured by loading test.

Fig. 7 Development of Young’s modulus of cement pastes calculated by using the results of ultrasonic pulse velocity measurements.

Fig. 8 Development of Poisson’s ratio of cement pastes calculated by using the results of ultrasonic pulse velocity measurements.

Fig. 9 Comparison of Young’s modulus obtained by loading test with Young’s modulus obtained by ultrasonic pulse velocity measurement.

this figure, while some variation can be seen, overall there is good agreement. With regard to Poisson’s ratio shown in Fig. 8, it tends to converge around the age of 7 days toward the value of 0.26 regardless of the water-cement ratio and cement mineral composition.

As described above, the physical properties show some variation over time according to the water-cement ratio and mineral composition, and in this study we attempted to evaluate the various mechanical properties with just one index encompassing these differences.

In this study, we calculated the gel-space ratio \( g/s \) expressed by Equation (5) from the phase compositions in the sealed state shown in Fig. 3, and adopted the evaluation of strength based on the gel-space ratio theory of Powers expressed by Equation (6) (Powers 1958).

\[
X = \frac{V_{\text{hyd}}}{V_{\text{hyd}} + V_{\text{pore}}} \quad (5)
\]

\[
\sigma = \sigma_0 X^\nu \quad (6)
\]

where \( X \) = gel-space ratio (vol./vol.), \( V_{\text{hyd}} \) = sum of
amounts of various hydration products (cm$^3$), $V_{pore}$ = total void volume (cm$^3$), $\sigma$ = strength (MPa), $\sigma_0$ = ultimate strength (MPa), and $N$ = material constant.

The gel-space ratio is the ratio of the amount of hydration product to the sum of the total void volume and amount of hydration product. In the present study, the skeleton of C-S-H in the saturated or sealed condition is assumed to be the same as that dried under 11% RH, even though some additional adsorption in the inner-layer is possible. This assumption is reflected by the fact that the water above 11% RH is easily evaporate under the drying process and can not be considered as a part of C-S-H structure (Allen et al. 2010). Correspondingly, the density of water in C-S-H above 11% RH is considered as 1.0 g/cm$^3$ by Young & Hansen (1986) and Setzer & Liebrecht (2007). Based on these results studies, we take adopted such assumption. In addition, we will not show the impact of individual cement hydrates and cement minerals on the physical properties, because we can not draw the significant results from the present data set. Nevertheless, the precise phase composition in cement paste is necessary to obtain the value of volume of solids, water, and voids.

Under ideal conditions where all voids are filled by gel (hydration product), $\sigma$ becomes $\sigma_0$, and the strength becomes either the theoretical ultimate strength or maximum ultimate strength. The $N$ value represents the dependence of strength on the gel-space ratio. In this hypothesis, it is considered that unhydrated cement does not contribute to strength, or alternatively, to collapse of the paste. This is reflected by the fact that hydration product has lower strength compared to unhydrated cement. This means that the collapse of cement paste is initiated from the hydration products phase, namely, the interfaces between cement hydrates, when as far as the the system in the cement paste is assumed to be composed of three phases, such as voids, hydration product phase, and unhydrated cement mineral phase.

Figure 10 shows the results for compressive strength as a function of the gel-space ratio. As shown in this figure, the high correlation between $g/s$ and strength $F_p$ is reproduced. With regard to the relationship between $g/s$ and strength, $N$ is distributed in the value range of 2.0 to 3.0 in the studies of Powers (1960), Taylor (1997), Osbaeck (1992), and Sakai (1998), but in this study, the value of $N$ is 3.9, which is higher than for any of the above-mentioned studies. This is due to the fact that because of differences in the preparation of the paste, the loading conditions, and the values used in the phase composition assessment, direct comparison of consistency with the constants in this study is not possible. But the assumption that the C-S-H in sealed condition is the same as that dried under 11% RH affects the amount of the solid volume and resultantly, may pose a large impact on the $N$ value.

Next, we examined Young's modulus. While a primary correlation between Young's modulus and $g/s$ is obtained for each mix proportion, there was no universal relationship with regard to W/C and cement type. By considering the interior of hardened cement paste consisting of unhydrated particles, hydrates, and voids, deformations in hardened cement paste are determined by the volume of hydration products and voids. This is why Young's modulus and $g/s$ have linear correlation.

Generally, Young's modulus and density are related by the equation of motion (Equation (7)).

$$\rho \frac{\partial^2 u}{\partial t^2} = E \frac{\partial^2 u}{\partial x^2}$$

(7)

Based on the fact that in a uniform body, Equation (7) holds true at any time and at any coordinates, density and Young's modulus have a linear correlation to each other.

Thus, evaluation of Young's modulus by the index consisting of density and $g/s$ yielded the high correlation shown in Fig. 11. As shown in that figure, the index obtained by multiplying density by $g/s$ can predict Young's modulus as a straight line regardless of the water-cement ratio, material age, and mineral composition of the cement.

This straight line has an $x$-intercept and does not pass through the origin. This is thought to be due to the fact that even though hydration products are produced, Young's modulus is not expressed without the formation of a structure that serves as the stress transfer path. Regarding this point, it is believed that the validity of this
equation can be further boosted in the development process of Young's modulus by accumulating data in the vicinity of the intercept in the future.

Next, let us consider Poisson's ratio. Plotting Poisson's ratio against g/s showed that evaluation on the same curve is possible, as shown in Fig. 12. The fact that Poisson's ratio could be evaluated from the gel-space ratio regardless of the water-cement ratio and cement types is considered to be due to the significantly higher rigidity of unhydrated cement particles than hydration products and voids, resulting in a relatively small amount of deformation that does not contribute to Poisson's ratio of hardened cement paste.

3.3 Water vapor adsorption test

Figure 13 shows the water vapor adsorption process data, and Fig. 14 presents the development of BET specific surface area of water vapor calculated from this data. The relationship between chemically bound water and the specific surface area was also examined in order to predict this trend from hydration. Figure 15 shows the data verified with regard to the correlation of chemically bound water at 11%RH and BET specific surface area of water vapor adsorption $S_{BET}$. As shown in this figure, it was reconfirmed that the relationship between the BET specific surface area of water vapor and chemically bound water amount is represented by a single curve, irrespective of the cement type and water-binder ratio. Moreover, from a different perspective, a bilinear trend with 0.2 g/g of chemically bound water as the boundary can be identified.

A discussion of the above follows. In this discussion, based on the assumption that C-S-H of hardened cement paste accounts for the greatest part of hydration products, we will discuss the behavior of hardened cement paste with a focus on C-S-H.

Based on the fact that the BET surface area of the water vapor adsorption isotherms of C-S-H are higher than that of nitrogen adsorption isotherms (Feldman and Sereda 1968; Odler 2003), water vapor is considered to be a highly hydrophilic chemical adsorption rather than physical adsorption determined from the physical surface structure of C-S-H (Feldman and Sereda 1968). On the other hand, based on the fact that according to previously
proposed structural models of C-S-H, structural water constituting the molecular structure of C-S-H occurs as hydroxy groups (e.g. Nonat 2004; Richardson 2004), adsorption sites for water vapor are considered to be located on the hydroxy groups of C-S-H, and thus there is a high correlation between the BET specific surface area of water vapor and the amount of chemically bound water as hydroxy groups in C-S-H.

Given the results of these tests in this respect, while the amount of adsorbed water is determined by the H$_2$O/Si ratio as a number of adsorption sites in a dry state at 105°C, which is the pre-treatment condition for the water vapor adsorption test, the amount of chemically bound water obtained from thermal analysis is determined by the H$_2$O/Si ratio, which is a function of the amount of desorption of adsorbed water at 11%RH and the amount of desorption of structural water caused by the production of siloxane bonds by the hydroxy groups. The BET specific surface area of water vapor and amount of chemically bound water are both considered to be functions of the hydroxy groups.

If the adsorption potential exerted on water molecules from the hydroxy groups at the C-S-H surface is constant, the amount of adsorbed water is determined solely by the amount of hydroxy groups, and the relationship between the BET specific surface area of water vapor and the amount of chemically bound water is considered to be linear. However, since the relationship between the two is curvilinear and not proportional, the fact that the adsorption potential from the hydroxy groups varies cannot be ignored. Considering that the initial hydration occurs in the interlayer spaces of C-S-H, it can be surmised that this variation is caused by the variation in overlapping effects of bonding (or adsorption) potential from both sides resulting from changes in interlayer spacing due to changes in the Ca/Si atomic ratio (Diamond 1964). It is generally known that the Ca/Si atomic ratio of C-S-H generated from synthesized C$_3$S, C$_2$S, and various cements varies depending on the hydration reaction (Kantro et al. 1962; Nishikawa and Suzuki 1994), and that the BET specific surface area increases as the Ca/Si atomic ratio of C-S-H decreases (Kantro et al. 1961; Bentur and Berger 1979). Based on this, the specific surface area of hardened cement paste is considered to be affected not only by the amount of C-S-H in the hardened cement paste, but also by the Ca/Si atomic ratio of C-S-H. The change over time of average Ca/Si atomic ratio calculated from the phase composition is shown in Fig. 16, where the Ca/Si atomic ratio shows a tendency to decline with time in all cases. The relationship between the BET specific surface area of water vapor and the amount of chemically bound water when the Ca/Si atomic ratio drops below 0.3 is considered below. For the relationship between the Ca/Si atomic ratio of C-S-H and the water vapor adsorption specific surface area $S_{H2O}$ (m$^2$/g), we used the following equation obtained from previously published work (Igarashi and Maruyama 2012). The relationship between the Ca/Si atomic ratio of C-S-H and $S_{H2O}$ obtained with the same technique as that of present study is shown in Fig. 17.

$$S_{H2O} = 234 - 297 \cdot \ln(Ca/Si) \quad (8)$$

The relationship between chemically bound water and $S_{H2O}$ at 11%RH or lower when the Ca/Si atomic ratio differs by 0.3 is shown in Fig. 18. As shown in this figure, the relationship between the two properties shifts toward the upper right when the Ca/Si atomic ratio decreases. When the effect of the decline of the Ca/Si atomic ratio
and the tendency for the specific surface area to increase due to hydration overlap, the slope becomes similar to that seen when the amount of bound water is 0.2 g/g or higher. Thus, it is considered possible to evaluate the relationship between chemically bound water and $S_{\text{H}_2\text{O}}$ on the same curve.

3.4 Thermal conductivity

Figure 19 shows the development of thermal conductivity of the hardened cement pastes. As shown in this figure, the thermal conductivity of hardened cement paste shows a tendency to slow down after increasing up to around the age of 7 days for all parameters. Further, after peaking around the age of 28 days, thermal conductivity tends to decline for some of the parameters. Focusing on differences in water-cement ratio, the thermal conductivity of hardened cement paste was confirmed to tend to be higher for W/C=0.40 compared with W/C=0.55. Moreover, looking at differences in cement type, the thermal conductivity of hardened cement paste was found to be almost the same for N and M, and tended to be lower for L. The possibility of evaluating the development of thermal conductivity of hardened cement paste through previously proposed rules of mixture was examined. Four rules of mixture were considered, namely the parallel model, which uses the arithmetic mean, the series model, which uses the harmonic mean, the series-parallel model (hereinafter, W&M model) (Woodside and Messmer 1961), and the geometric mean model (Deguchi model) (Deguchi et al. 1995). The equations of each model are shown below (Eqs. (9) to 12)).

$$\lambda = V_s \lambda_s + V_l \lambda_l + V_g \lambda_g$$  
(9)

$$\lambda = \frac{1}{\frac{V_s}{\lambda_s} + \left(V_l + V_g\right)^{-1}}$$  
(10)

$$\lambda = a + b \frac{\lambda_s}{\lambda_l}$$  
(11)

$$\lambda = \frac{1}{V_s} \left[V_s \lambda_s + (1-V_s) \lambda_l\right]^{\frac{V_s}{a}} \cdot \lambda_l^{\frac{1-V_s}{d}}$$  
(12)

where $V_s =$ volume ratio of solid phase (vol./vol.), $V_l =$ volume ratio of liquid phase (vol./vol.), $V_g =$ volume ratio of gas phase (vol./vol.), $\lambda_s =$ thermal conductivity of solid phase (W/(m·K)), $\lambda_l =$ thermal conductivity of liquid phase (≈0.6 W/(m·K)), $\lambda_g =$ thermal conductivity of gas phase (≈ 0.026 W/(m·K)), and $a$ to $d$ are constants.

Rule of mixture evaluation using each of the above-mentioned models for the solid, liquid, and gas phases was attempted.

The evaluation procedure consisted in subtracting the contributions of the liquid phase and the gas phase from the experimental values of thermal conductivity of hardened cement paste. With regard to the contribution to thermal conductivity of the solid phase thus obtained, the average of all the plots was used as the solid phase thermal conductivity. Using the identified solid phase thermal conductivity and the thermal conductivities of the liquid phase and gas phase, the thermal conductivity of hardened cement pastes was estimated and the results were compared with the experimental values. Table 4 lists the estimated solid phase thermal conductivity val-
ues for each rule of mixture, and Figure 20 shows a comparison of the predicted thermal conductivity of hardened cement paste using the obtained solid phase thermal conductivity results with the experimental values. As shown in Fig. 20, the parallel model and W&M model are found to be well suited as mixture models owing to their high coefficient of determination.

These results are thought to be attributable to the fact that the thermal conductivity of hardened cement paste occurs mostly as parallel conductivity of the solid phase and liquid phase (parallel model), and conductivity in series of the solid phase and liquid phase (series model) does not occur to any great extent. Given that the structure of hardened cement paste is formed by the solid phase, this can be said to be reasonable. For the purpose of simple evaluation, the parallel model appears to be a sufficiently useful evaluation method.

4. Conclusion

As a basic research for predicting the properties of concrete, this study experimentally obtained the changes in phase composition for the hydration process in two water-cement ratios and three types of Portland cement and the resultant physical properties, i.e. compressive strength, Young’s modulus, Poisson’s ratio, water vapor adsorption specific surface area, and thermal conductivity. Further, beneficial empirical formulas correlating phase compositions with physical properties of hardened cement paste at sealed condition were proposed, and the backgrounds of these empirical formulas were discussed.

Followings are the summary of the obtained experimental results:
- Compressive strength of hardened cement paste can be evaluated as a function of gel to space ratio, which is originally proposed by Powers.
- Young’s modulus of hardened cement paste was a function of the product of density and gel to space ratio.
- Poisson’s ratio of hardened cement paste was also a function of gel to space ratio.
- Water vapor BET surface area of hardened cement dried at the saturation to the equilibrium with saturated LiCl solution for 2 weeks resulted in a function of chemically bound water.
- Thermal conductivity of hardened cement paste at sealed condition is well-predicted by the parallel model considering the volume fraction of solid, void, and liquid.

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References


