

## Effect of Curing Temperature and Water to Cement Ratio on Hydration of Cement Compounds

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### 1. Introduction

In order to estimate and evaluate the physical properties of cementitious materials, it is necessary to accurately grasp the proportion of each mineral in cement and determine its hydration rate, which changes depending on various environmental factors. However, it is difficult to quantify accurately the phase composition of cement paste by traditional analysis. In regard to the proportion of each mineral in cement, it is known that the proportion of a mineral determined by general practice using the Bogue calculation can differ from the actual value, as this method is affected by the calcination degree of clinkers and the proportions of trace constituents [1]. Also, the point count method using a polarization microscope requires substantial skill for observation, being prone to individual differences. The powder X-ray diffraction/internal standard method carried out by adding an internal standard is difficult to apply to quantification of all minerals, having an accuracy problem because of peak overlapping. In regard to the evaluation of hydration reactivity, qualitative comparison of the overall reaction based on the amount of bound water and rate of heat liberation is generally practiced, as these are relatively easy to carry out. On the other hand, several reports have been published regarding evaluation by quantification of the hydration rate of each mineral [2,3], with very little data being available. Data accumulation is therefore vital for formulating a hydration model [4] for accurately predicting the physical properties of a cementitious material.

Powder X-ray diffraction/Rietveld analysis [5] (hereafter referred to as Rietveld analysis) has been utilized in recent years as a technique for quantifying the crystal mineral phase of e.g., cement minerals [6]. It is also beginning to be used for quantification of amorphous substances [7] and hydration analysis of hydrated cement paste [8,9], reportedly providing accurate quantification results with no individual differences in a short time, once the analysis condition for each cement were determined.

In this study, the authors therefore carried out quantification of residual minerals and hydrates in cement paste using the Rietveld analysis method, its accuracy was verified by Hoshino et al [9]. Based on these results, as well as evaluation of the effects of curing temperature and water to cement ratio (W/C) on the hydration, the changes in the phase

composition of cement were calculated to investigate the changes in the C-S-H composition.

## 2. Experimental procedure

### 2.1 Materials

The chemical composition of ordinary portland cement used in this experiment is given in Table 1. Table 2 gives its density, specific surface, and mineral compositions determined by Bogue calculation and Rietveld analysis. There are slight differences between the mineral compositions determined by Bogue calculation and Rietveld analysis.

### 2.2 Experiment factors

The factors of this experiment are given in Table 3. These include three levels of W/C: 50%, 35%, and 25%; three levels of mixing/curing temperatures: 283 K, 293 K, and 313 K; seven test ages: 1, 3, 7, 28, 91, 190, and 365 days. The sample with W/C of 25% was added with superplasticizer and tested only at 293 K.

### 2.3 Measurements and analysis of hydration

Analysis samples were prepared as follows: Mix the materials at the specified temperature and seal-cure until the specified age. Cut the specimen to an appropriate size with a diamond cutter and finely pulverize

Table 1 Chemical composition of cement

Ignition loss [%]	Chemical Composition [%]								
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl
2.40	20.23	5.39	3.04	64.64	0.92	1.91	0.30	0.31	0.025

Table 2 Density, specific surface area, and mineral composition of determined by Bogue Equation and Rietveld analysis

Density [g/cm <sup>3</sup> ]	Surface Area [cm <sup>2</sup> /g]	Bogue Composition [%]			
		C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
3.16	3300	63.3	10.3	9.1	9.2

Rietveld Method [%]								
C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaSO <sub>4</sub> ·1/2H <sub>2</sub> O	CaCO <sub>3</sub>	MgO	f-CaO
58.8	17.2	7.0	9.9	0.43	2.01	3.77	0.77	0.39

Table 3 Experimental factors

W/C ratio[%]	50, 35, 25 (only 293K)
Temperature[K]	283, 293, 313
Curing time[days]	1, 3, 7, 28, 91, 190, 365

with acetone using a disk mill. After separating the powder from acetone by suction filtration, dry the sample for approximately two weeks in an environment of 15%RH, to obtain a hydration analysis sample. The powder X-ray diffraction was measured under the following conditions: The X-ray source: Cu-K $\alpha$ ; tube voltage: 50 kV; tube current: 250 mA; scan field: 2 (theta) = 5 to 65 deg; step interval: 0.02 deg; and scan speed: 2 deg/min. The TOPAS software from Bruker AXS Inc. was used for Rietveld analysis. The subjects of quantification were cement minerals and hydrates, such as C<sub>3</sub>S, C<sub>2</sub>S, cubic C<sub>3</sub>A, orthorhombic C<sub>3</sub>A, (total C<sub>3</sub>A), C<sub>4</sub>AF, MgO, free-CaO, CaCO<sub>3</sub>, CaSO<sub>4</sub>.2H<sub>2</sub>O, CaSO<sub>4</sub>.1/2H<sub>2</sub>O, Ca(OH)<sub>2</sub> (CH), C<sub>3</sub>A.3CaSO<sub>4</sub>.32H<sub>2</sub>O (AFt), C<sub>3</sub>A.CaSO<sub>4</sub>.12H<sub>2</sub>O (AFm), C<sub>3</sub>A.CaCO<sub>3</sub>.12H<sub>2</sub>O (Mc), and C<sub>3</sub>A.1/2CaCO<sub>3</sub>.1/2Ca(OH)<sub>2</sub>.12H<sub>2</sub>O (Hc), as well as a-Al<sub>2</sub>O<sub>3</sub> mixed with the analysis samples at 10% by weight as the internal standard. Mc and Hc [10] were selected because the cement used in this experiment contained limestone powder. Structural models for clinker minerals (C<sub>3</sub>S, C<sub>2</sub>S, cu-C<sub>3</sub>A, or-C<sub>3</sub>A, and C<sub>4</sub>AF) were taken from the NIST Technical Report [11], Those for calcite, gypsum, bassanite, CH, AFt, AFm, Mc, and corundum were taken from ICSD Database [12]. Note that the value for CH was separately determined by Thermal Gravimetry (TG), as the quantified values by Rietveld analysis (XRD) was about 3% lower than TG, it also reported by Midgley [13]. All amorphous substances were assumed to be C-S-H in this study and calculated by Eq. (1) from the quantitative value of the internal standard of Al<sub>2</sub>O<sub>3</sub> [14].

$$A = \{100 (S_R - S)\} / \{S_R (100 - S) / 100\} \quad \text{Eq. (1)}$$

where, A = proportion of amorphous substance (%), S = mixing rate of Al<sub>2</sub>O<sub>3</sub> (%), S<sub>R</sub> = quantitative value of Al<sub>2</sub>O<sub>3</sub> (%)

### 3. Verification of the accuracy of quantification by Rietveld analysis

On carrying out hydration analysis by the Rietveld analysis, its accuracy was verified.

#### 3.1 Reaction rate of cement compounds determined by internal standard method and Rietveld analysis

In regard to the reaction rate of each mineral in cement paste, the accuracy of quantification by Rietveld analysis was verified by comparison with the values determined by the internal standard method, which is a general quantification method in XRD analysis. Figure 1 shows the quantification results of C<sub>3</sub>S and C<sub>3</sub>A, two of the major compounds of cement, by the internal standard method and Rietveld analysis. The Rietveld analysis is found to provide an accuracy comparable to that of the internal standard method, though with a slight scatter in the low reaction rate range.

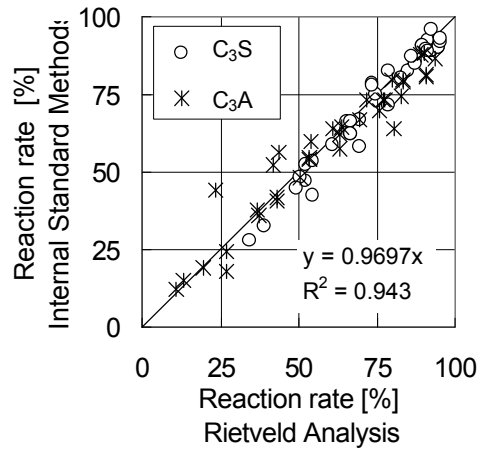


Fig.1 Comparison of reaction rate of C<sub>3</sub>S and C<sub>3</sub>A by Rietveld analysis with Internal standard Method

### 3.2 Amount of bound water determined by ignition loss and Rietveld analysis

Not only cement minerals but also hydration products can be quantified by Rietveld analysis. Accordingly, the amount of bound water in each hydrate was appropriately assumed based on the literature [15,16], and the amount of bound water in the hydration process of cement paste was calculated by Rietveld analysis. The obtained values were then compared with the amount of bound water determined by ignition loss (weight loss when heated to 1273K), which is generally practiced for the evaluation of hydration, thereby verifying the accuracy of quantification of the entire reaction system of cement by Rietveld analysis. Table 4 gives the assumed compositions of samples dried at 15%RH and D-dry conditions. Whereas measurement by the ignition loss method was carried out under both drying conditions, Rietveld analysis of the cement mineral phases and hydrates was conducted only on samples dried at 15%RH. The amount of bound water under D-dry was calculated based on the analysis results at 15%RH on the assumption that water is bound at a ratio as given in Table 4.

Figure 2 compares the amount of bound water determined by the ignition loss method and Rietveld analysis. The amount of bound water under 15%RH and D-dry conditions is accurately predicted by Rietveld analysis, suggesting that this analysis method accurately quantifies the hydrates in the cement hydration process.

It was thus demonstrated that both cement minerals and hydrates in the cement hydration process can be quantified by Rietveld analysis.

Table 4 Molecular weight, Density, and Water contents for phases in cement paste dried at 11%RH and D-dry conditions

Name	Molecular weight	Density	H <sub>2</sub> O/Ca	Molecular weight	Density	H <sub>2</sub> O/Ca
	[g]	[g/cm <sup>3</sup> ]	ratio	[g]	[g/cm <sup>3</sup> ]	ratio
11%RH <sup>*1</sup>			D-dry			
C-S-H <sup>*2</sup>	200.5	2.18 <sup>*3</sup>	1.47	184.2	2.70 <sup>*3</sup>	0.94
CH	74.1	2.24	1.00	74.1	2.24	1.00
Calcite <sup>*4</sup>	100.1	2.30	1.00	100.1	2.30	1.00
AFt	1251.5	1.73	5.33	894.8	2.38	2.00
AFm	622.5	1.99	3.00	543.3	2.40	2.00
Mc	586.5	1.99	3.00	514.4	2.40	2.00
Hc	573.5	1.99	3.12	501.4	2.40	2.13

\*1 15%RH(this study) \*2 11%RH : C<sub>1.7</sub>SH<sub>2.5</sub>, D-Dry : C<sub>1.7</sub>SH<sub>1.6</sub>

\*3 Exclusive of Gel Porosity \*4 CO<sub>2</sub>/Ca ratio

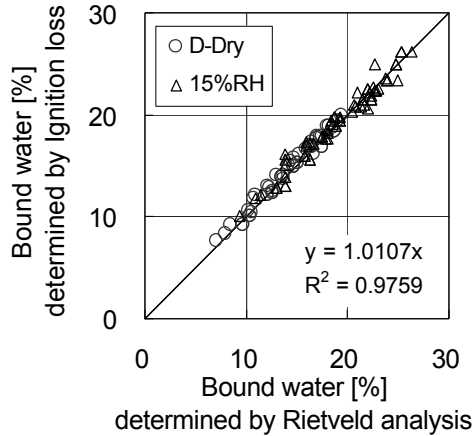


Fig.2 Comparison of the amount of bound water calculated by Rietveld analysis with determined by Ignition loss (Dried at 15%RH and D-dry conditions)

#### 4. Results and discussion

##### 4.1 Reaction rate of cement minerals and hydration rate of cement

Figure 3 shows the reaction rates of cement compounds in cement pastes with W/C of 50% at different curing temperatures of 283 K, 293 K, and 313 K, as well as pastes at a curing temperature of 293 K with different W/C of 50%, 35%, and 25%.

When comparing the hydration rates of the calcium silicate phase, the reaction rates of C<sub>3</sub>S at 283 K, 293 K, and 313 K at an age of 1 day are around 40%, 60%, and 80%, respectively, with all samples with W/C of 50% eventually converging to approximately 90%. The reaction rate of C<sub>2</sub>S is low at early ages when compared with that of C<sub>3</sub>S but increases in the period between 7 and 91 days. The reaction rates of samples at 283 K

and 293 K were 80% and 90%, respectively, at 365 days. Their slopes suggest that these will eventually attain 100%.

When comparing the hydration rates of the calcium aluminate phase, the reaction rates of samples cured at high temperatures are higher until 7 days, but that of samples cured at 313 K stops increasing after 7 days, being stagnant at 70%. When cured at 283 K and 293 K, approximately 90% of  $C_3A$  has reacted by 365 days. The reaction rate of  $C_4AF$  is low when compared with other minerals, showing similar results similar to those by Asaga et al. [3], which reported that only 40% of  $C_4AF$  reacted in samples with a W/C of 30% cured at 293 K. Accordingly, reaction of the calcium aluminate phase is significantly retarded by high temperature curing in contrast to the tendencies of the calcium silicate phase. This differs from the temperature dependence reported in the literature. This can be attributed to the significant effect of the high temperature of not only the curing temperature but also the mixing temperature in the present experiment.

The reaction rates of all cement minerals with W/C of 50%, 35%, and 25%, excepting  $C_3S$  and  $C_2S$  with W/C of 25%, are of the same level up to an age of 7 days but decrease thereafter as the W/C decreases. This tendency is particularly evident after 28 days. When comparing the ultimate reaction rates of these minerals, the losses in the reaction rate due to reductions in the W/C of  $C_3S$ ,  $C_3A$ , and  $C_4AF$  are similar, whereas  $C_2S$  is strongly affected by the reductions in the W/C. While the ultimate reaction rate of  $C_2S$  is 90% with W/C of 50%, it is 35% when the W/C is 25%. This is presumably because the effect of reductions in water and spaces for deposition necessary for hydration is stronger on  $C_2S$ , whose reaction actively progresses at later ages.

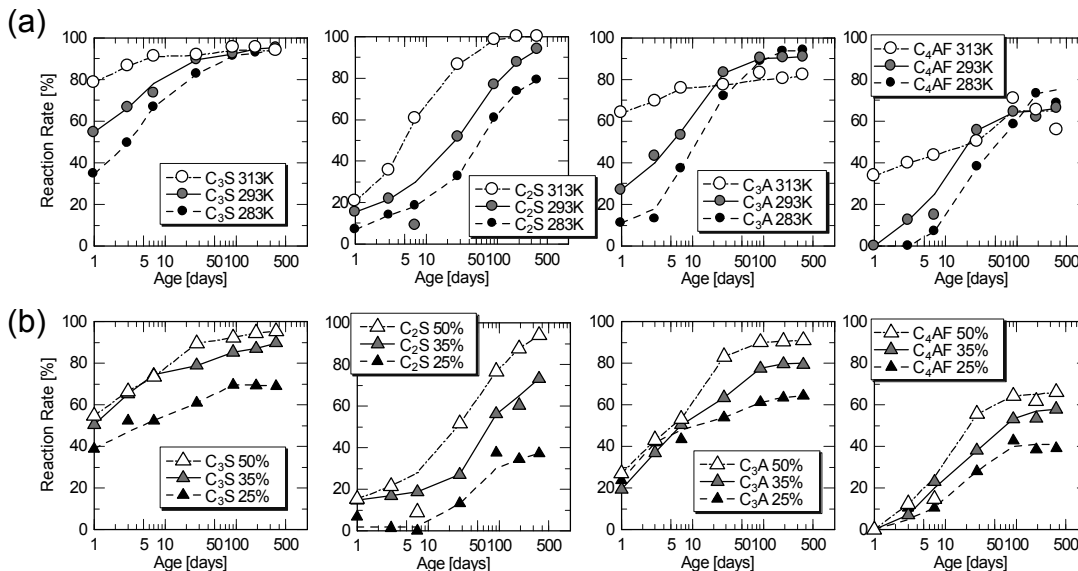


Fig.3 Reaction rate of cement compound calculated by Rietveld analysis (a) W/C50%, cured at 283K, 293K and 313K, (b) W/C50%, 35% and 25% cured at 293K

Figure 4 shows the hydration rates of cement as a whole calculated from the residual proportions of  $C_3S$ ,  $C_2S$ ,  $C_3A$ , and  $C_4AF$ . Similarly to the results of the reaction rate of each mineral, the tendencies of acceleration by high temperature curing, retardation by low temperature curing, and reduction in the reaction rate by reduction in the W/C are recognized. Acceleration and retardation of cement reaction depending on the curing temperature are evened out at 190 days at a reaction rate of 85-90%, and the ultimate reaction rate of high temperature curing samples tends to become slightly lower than the others. The effect of losses in the water and deposition spaces necessary for hydration due to a low W/C is recognized after an age of 3 and 7 days with a W/C of 25% and 35%, respectively. The reaction rates fail to reach 100% at the end of 365-day testing even with W/C of 50%, ending up at around 90%, 80%, and 60% with W/C of 50%, 35%, and 25%, respectively.

Rietveld analysis is thus found to be capable of quantifying the dependence of hydration of each cement compound on the temperature and W/C.

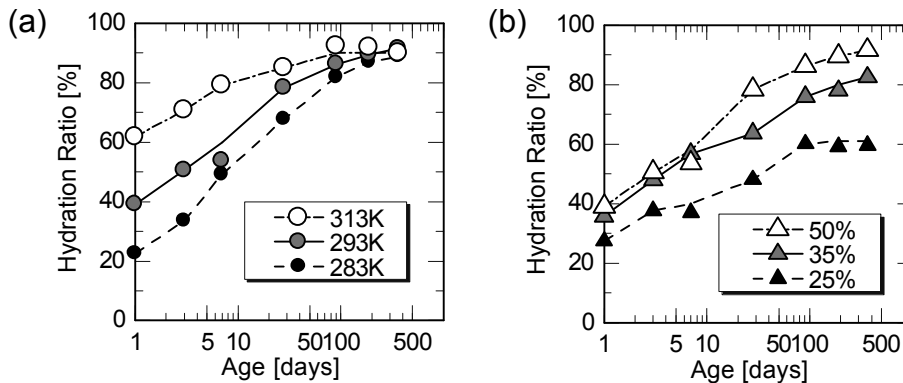


Fig.4 Hydration ratio of cement calculated by Rietveld analysis ( (a) W/C50%, cured at 283K, 293K, and 313K, (b) W/C50%, 35%, 25% cured at 293K)

#### 4.2 Proportions of hydrates

Table 5 gives the results of quantification of residual unhydrated cement and hydration products at 28 days by Rietveld analysis. The residual unhydrated cement refers to the sum of  $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ , gypsum, etc.; CH and AFt denote the proportions of respective hydration products; AFm denotes the sum of AFm, Mc, and Hc hydrates; and C-S-H denotes the proportion of amorphous substances determined by  $\alpha\text{-Al}_2\text{O}_3$ , the internal standard.

The proportions of CH and C-S-H, which are the hydration products of the calcium silicate phase, are higher with a higher curing temperature and a higher W/C at 28 days, showing similar tendencies as the reaction rates of

C<sub>3</sub>S and C<sub>2</sub>S. Table 5 gives the CaO/SiO<sub>2</sub> mole ratio of C-S-H calculated from the mass balance of CaO and SiO<sub>2</sub>, which was determined from the proportion of CH and the reaction rate of C<sub>3</sub>S and C<sub>2</sub>S. The C/S ratio of W/C50%-293K at 28 days is 1.79 and tends to increase as the W/C decreases. The C/S ratio calculated from mass balance is similar to 1.4 to 2.0, the value of measurement by EPMA, etc. [17,18].

The sum of the proportions of AFt and AFm resulting from reaction of the calcium aluminate phase tends to increase as the curing temperature decreases and as the W/C increases. The proportions of AFt and AFm produced in samples cured at a high temperature are smaller than those cured at lower temperatures due to stagnation in reaction of C<sub>3</sub>A and C<sub>4</sub>AF, and AFm accounted for most of these products at 1 day. Whereas the effect of W/C scarcely appears on the AFt production, with the residual AFt being around 3% in all samples. The AFm production increases as the W/C increases, it correlates with reaction rate of C<sub>3</sub>A and C<sub>4</sub>AF.

Accordingly, Rietveld analysis is found to be capable of quantifying the effects of the curing temperature and W/C on the proportions of hydration products.

Table 5 Relative mass of each phases in cement paste (at 28days)

Name	Cement	CH	AFt	AFm	C-S-H (C/S)
50%-283K	33.1	16.9	4.5	9.3	36.1 (1.79)
50%-293K	22.6	17.5	2.9	8.2	48.8 (1.79)
50%-313K	17.4	18.9	0.2	7.4	56.1 (1.74)
25%-293K	52.6	11.0	3.5	3.4	29.6 (1.95)
35%-293K	37.2	15.2	3.6	5.3	38.7 (1.86)
50%-293K	22.6	17.5	2.9	8.2	48.8 (1.79)

#### 4.3 Calculation of phase composition changes

The changes in the phase composition of cement paste samples [vol.%] were calculated from the proportions of cement minerals and hydrates quantified by Rietveld analysis, with which the capillary pore volume was calculated by Rietveld analysis based on the relationship given in Eq. (2). The densities of minerals and hydrates in D-dry conditions were set as given in Table 4, referring to the results by Taylor [15] and Tennis et al [16]. The gel pore volume was assumed to be 28% of the volume of all hydration products based on the assumption of Powers [19]. The hydration shrinkage associated with the hydration process was calculated using Eqs. (3) and (4) [20].

Figure 5 shows the phase composition changes with W/C of 50% and 25% (vol.%). It was confirmed that the changes in the phase composition can be followed with a certain accuracy (multiple correlation coefficient R<sup>2</sup> = 0.87) by comparing the capillary pore volume of D-dry samples measured using a mercury intrusion porosimetry and the pore volume



determined from Rietveld analysis, while assuming the specific gravity of hydrates and the chemical shrinkage based on the literature.

$$V_{C(0)} + V_{W(0)} = V_{uc(t)} + V_{hyd(t)} + V_{CSH(t)} + V_{GP(t)} + V_{cap(t)} + V_{HS(t)} \quad \text{Eq. (2)}$$

Where,  $V_{i(t)}$  = Volume of  $i$  at age  $t$  (vol.%),  $C$ : Cement,  $W$ : Water,  $uc$ : Unhydrated Cement,  $hyd$ : HYDRates except C-S-H,  $CSH$ : C-S-H,  $GP$ : Gel Pores,  $cap$ : CAPillary pore,  $HS$ : Hydration Shrinkage,  $(0)$ : at mixing time

$$V_{HS(t)50} = b_0 + b_1 a_{C3S(t)} (\%C_3S) + b_2 a_{C2S(t)} (\%C_2S) + b_3 a_{C3A(t)} (\%C_3A) + b_4 a_{C4AF(t)} (\%C4AF) \quad \text{Eq. (3)}$$

Where,  $V_{HS(t)50}$  = hydration shrinkage of cement paste with W/C50% at age  $t$ ,  $a$  = reaction rate (%),  $(\%i)$  = amount of each cement compound( $i$ ),  $b_{0-4}$  = Experimental constants ( $b_0 = -0.3333$ ,  $b_1 = 0.0852$ ,  $b_2 = 0.0373$ ,  $b_3 = 0.2588$ , and  $b_4 = -0.0462$ )

$$V_{HS(t)50} = V_{HS(t)WC} ((WC+1/r_c)/(0.5+1/r_c)) \quad \text{Eq. (4)}$$

Where  $V_{HS(t)WC}$  = hydration shrinkage of cement paste with a W/C(WC) at age  $t$  (vol.%),  $r_c$  = specific gravity of cement, WC = water to cement ratio

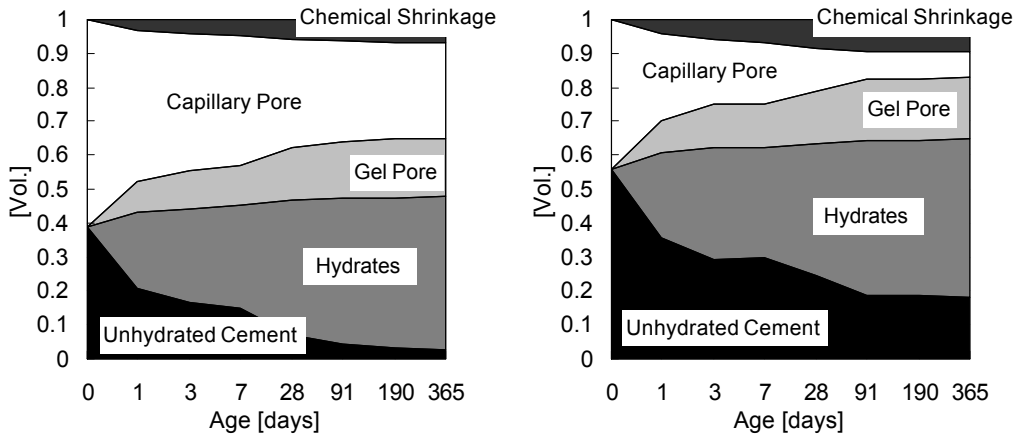


Fig.5 Relative Volume of Each Phase [Vol.%] (Left: W/C50%-293K, Right: W/C25%-293K)

#### 4.4 Effects of curing temperature and W/C on C-S-H composition

It is pointed out that the composition of C-S-H varies depending on the W/C and curing temperature [21], the calculation of C/S in C-S-H described in Section 4.2 and phase composition changes in Section 4.3 also suggested that the composition of C-S-H varies depending on the curing temperature and W/C. Accordingly, the effects of the curing

temperature and W/C on the density and gel pore volume of C-S-H were investigated, beginning with the assumptions as described below. Back analysis was carried out to investigate the changes in the gel pore volume by adjusting the gel pore volume in C-S-H so as to fit the capillary pore volume determined by Rietveld analysis to the value measured with a mercury intrusion porosimetry. This was based on the assumption that the capillary pore volume measured with a mercury intrusion porosimetry accurately expresses the pore volume in cement paste and that the volumes of cement minerals, hydrates in cement paste are true values with an exception of  $V_{GP}$  (Volume of gel pores) in Eq. (2).

Table 6 gives the calculated gel pore volume in all hydrates and C-S-H, and Fig.6 gives the calculated density of C-S-H when the gel pore saturated with water. The gel pore volume in all hydrates in D-dry samples with W/C of 50% and 35% ranges from 0.28 to 0.30, being similar to the assumption value of Powers [19]. By calculation from the C-S-H production (mass %), gel pore volume (vol. %), and the specific gravity of C-S-H, the density of C-S-H including gel pores ranges from 1.5 to 1.9, and its density under water saturated condition ranges from 1.8 to 2.2, being similar to 1.95, the result by Taylor [22]. It was therefore found that the assumptions in this analysis are correct and that the proportions of C-S-H, which is amorphous, and gel pores can be accurately quantified by Rietveld analysis. Note that hardened C-S-H contained approximately 35 to 45% gel pores, which decreased as the curing temperature increased and as the W/C decreased. It was confirmed that the changes in the density of C-S-H slightly scattered up to an age of 7 days but increased thereafter as hydration proceeded.

Table 6 Gel pore volume in all hydrates and C-S-H (Vol.% / Vol.%)

	$V_{GP}/(V_{hyd}+V_{CSH}+V_{GP})$			$V_{GP}/(V_{CSH}+V_{GP})$		
	283K	293K	313K	283K	293K	313K
W/C50%	0.281	0.295	0.292	0.434	0.431	0.391
W/C35%	0.310	0.288	0.287	0.453	0.406	0.382
W/C25%	-	0.242	-	-	0.344	-

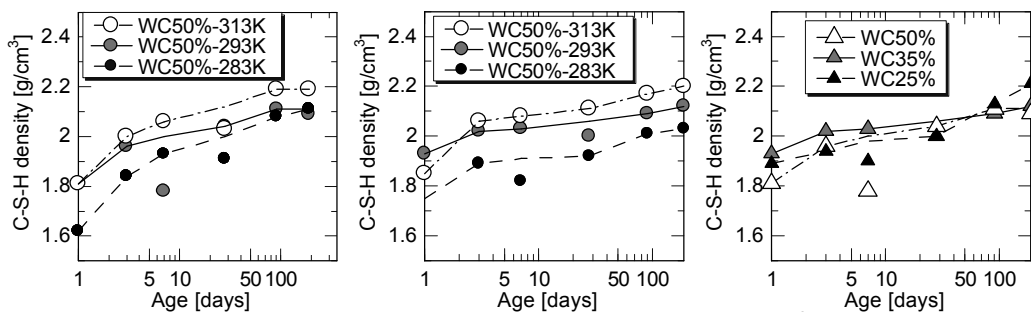


Fig.6 density of C-S-H under saturated conditions ( $g/cm^3$ )

## 5. Conclusions

Based on Rietveld analysis to quantify the reaction rate of cement minerals and the proportions of hydration products, the authors investigated the dependence of hydration on temperature and W/C, while calculating the changes in the phase composition of hardened cement and investigating the changes in the composition of C-S-H. The following were found:

(1) The proportions of residual minerals and hydration products in the process of cement hydration were quantified with a certain accuracy by Rietveld analysis.

(2) There are two types of temperature dependence of the hydration rates of cement minerals. With one type including the calcium silicate phase, the reaction rate varies depending on the curing temperature but ultimately converges to a certain level. With the other type including the calcium aluminate phase, the reaction rate of samples cured at a high temperature is high at early ages but becomes retarded at later ages, ultimately being exceeded by samples cured at a low curing temperature.

(3) The proportions of CH and C-S-H, which are produced in the calcium silicate phase, increase as the curing temperature and as the W/C increases. The proportions of AFt and AFm, which are hydrates in the calcium aluminate phase, are affected by the curing temperature and W/C, respectively.

(4) The calculation of the changes in the phase composition of cement paste based on the quantification of all minerals and hydrates revealed that curing at a high temperature and mixing with a low W/C reduce the gel pore volume and increase the density of C-S-H.

## References

- [1] G. Yamaguchi, S. Takagi, The analysis of Portland Cement Clinker, Proc. 5th Int. Symp. on the Chem. Cem., Vol.1, 1968, pp.181-218
- [2] L.E. Copeland, D.L. Kantro, George Verbeck, Chemistry of Hydration of Portland Cement, 4th Int. Symp. on the Chem. Cem., Vol.1, 1960, pp.429-465
- [3] K. Asaga, M. Ishizaki, S. Takahashi, K. Konishi, T. Tsurumi, M. Daimon, Effect of Curing Temperature on the Hydration of Portland Cement Compounds, 9th Proc. of the Int. Cong. on the Chem. Cem., Vol.4, 1992, pp.181-187
- [4] I. Maruyama, T. Noguchi, T. Matsushita, Prediction of Adiabatic Temperature Rise in Portland Cement Concrete Using Computational Cement Based Material Model, Journal of structural and construction engineering (transactions of AIJ), 600, 2006.2, pp.1-8 (in Japanese)
- [5] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, Journal of applied Crystallography, Vol.2, 1969, pp.65-71
- [6] G. Walenta, T. Fullmann, M. Gimenez, I. Leroy, R. Friedle, D. Hartung, C. Lauzon, D. Decary, Quantitative Rietveld analysis of cement and clinker, International Cement Review, June 2001, pp.51-54

- [7] T. Westphal, G. Walenta, M. Gimenez, E. Bermejo, T. Fullmann, K. Scrivener, H. Pollmann, Characterisation of cementitious materials - PART III, International Cement Review, July 2002, pp.47-51
- [8] K.L. Scrivener, T. Fullmann, E. Gallucci, G. Walenta, E. Bermejo, Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods, Cem. Concr. Res., 34, 2004, pp.1541-1547
- [9] S. Hoshino, K. Yamada, H. Hirao, Analysis of hydration and strength development of cement containing blast furnace slag and limestone powder by using XRD/Rietveld method, Journal of Advanced Concrete Technology, Vol.4, No.3, 2006, 357-367
- [10] C Vernet, Noworyta, Mechanisms of Limestone Fillers Reactions in the System  $\{C_3A-C\bar{S}H_2-CH-C\bar{C}-H\}$ : Competition Between Calcium Monocarbo- and Monosulfo- Aluminate Hydrates Formation, 9th Int. Cong. on the Chem. of Cem., Vol.4, 1992, pp.430-436
- [11] P. Stutzman, S. Leigh, NIST Technical Note 1441-Phase Composition Analysis of the NIST Reference Clinkers by Optical Microscopy and X-ray Powder Diffraction, 2002, pp.34-43
- [12] Fachinformationszentrum Karlsruhe and National Institute of Standards and Technology, Inorganic Crystal Structure Database, ICSD., 2006, <http://icsd.ill.fr/icsd/index.html>
- [13] H.G. Midgley, The Determination of Calcium Hydroxide in Set Portland Cements, Cem. Concr. Res., Vol.9, 1979, pp.77-82
- [14] R.C. Jones, C.J. Babcock, W.B. Knowlton, Estimation of the Total Amorphous Content of Hawaii Soils by Rietveld Method, Soil Science Society of America Journal, Vol64, 2000, pp.1100-1108
- [15] H.F.W. Taylor, Cement Chemistry, Academic Press, New York, 1990
- [16] P. D. Tennis, H. M. Jennings, A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes, Cem. Concr. Res., 30, 2000, pp.855-863
- [17] H.F.W. Taylor and D.E. Newbury, An Electron Microprobe Study of A Mature Cement Paste, Cem. Concr. Res., 14, 1984 pp.565-573
- [18] G.W. Groves, P.J. Le Sueur, W. Sinclair, Transmission Electron Microscopy and Microanalytical Studies of Ion-Beam-Thinned Sections of Tricalcium Silicate Paste, Journal of the American Ceramic Society, 69, No.4, 1986, pp.353-356
- [19] T.C. Powers, Discussion of Cement Hydration in Relation to the Curing of Concrete, Proc. of Highway Research Board 27, 1947, 178-188
- [20] T. Kasai, Y. Baba, S. Iwasa, Influence of Mineral Composition and Grading of Cement on Chemical Shrinkage of Cement Paste, Cement Science and Concrete Technology (Japan), No.53, 1999, pp.213-220
- [21] K.V. Breugel, Simulation of hydration and formation of structure in hardening cement-based materials, Ph.D thesis 2nd ed., TU Delft, 1997
- [22] H.F.W. Taylor, Chemistry of Cement Hydration, 8th Int. Cong. on the Chem. Cem., Vol.I, 1986, pp.82-110