- Technical Paper -

HYDRATION PROCESS AND DEVELOPMENT OF MECHANICAL PROPERTIES OF EUROPEAN-PRODUCED TYPE I CEMENT

Jiři RYMEŠ[1], Risako TANAKA[2], Ippei MARUYAMA[3]

ABSTRACT

Phase composition of cement paste of two different w/c ratios prepared from a European Type I cement was investigated through powder X-ray diffraction and subsequent Rietveld analysis at an early age of the material and the results were confirmed by thermal gravimetric analysis. Furthermore, mechanical properties of the material were measured on cylindrical specimens and based on microstructural properties obtained from the phase composition analysis, a relationship between gel/space ratio and compressive strength was found. Presented results are consistent with previous results of Japanese Portland cement systems.

Keywords: Portland cement, compressive strength, elastic modulus, XRD, Rietveld method, TG-DTA, gel/space ratio

1. INTRODUCTION

Cement paste provides an adhesive substance for bonding of aggregate into concrete, a stone-like material, which finds its application in a broad range of construction works. Because of its crucial role, the physical properties of cement paste, such as strength or elastic modulus, directly influence the behavior of the whole medium and subsequently of the whole structure. If those key properties are known, construction process can be optimize to obtain the ideal construction speed without any negative influence on the final qualities of the structure. Therefore, a great significance needs to be given to the investigation of the hydration process of cement paste at its early ages.

In the middle of the 20th century, a complex research of cement paste and concrete properties was done by Powers. A gel to space (g/s) ratio was proposed [1] and later modified [2] for predicting mechanical properties of cement paste based on its microstructural characteristics. Over the years, a broad set of experimental data obtained by different methods has been published by multiple researches e.g. [2] - [4], [6], [7] - [9].

In this paper, analysis results of cement paste prepared from European-produced ordinary Portland cement are presented and compared with previously published data [9]. Investigated cement paste was mixed with two different water to cement ratios (w/c) and its composition was measured by the X-ray diffraction (XRD) method and a thermogravimetric/differential thermal analyzer (TG-DTA) while mechanical properties, such as compressive strength and elastic modulus, were measured through compression loading test. W/c ratios of 0.40, as a lower one, and 0.52, as a higher one, were chosen for sample preparation.

2. EXPERIMENTAL RESEARCH

2.1 Sample preparation

European-produced Type I cement labeled as CEM I 52.5 N (ordinary Portland cement, 52.5 MPa standard strength, normal early strength) was used for the experimental analysis. Properties of the material are listed in Table 1. Cement pastes for samples were mixed using a dual centrifugal mixer. Mixing time of 0.40 w/c ratio was 2 minutes and one-step procedure was applied while cement paste with 0.52 w/c ratio was mixed in 2 steps. Firstly, the paste was mixed to 0.40 w/c ratio, then additional water was added to the mixture to obtain the desired w/c ratio and the material was mixed for another 2 minutes. Prior to the mixing, dry cement powder was stored in sealed conditions in a temperature control room (20 ± 2 °C) as well as deionized water used for mixing. To prevent bleeding, before pouring into molds, cement paste was being remixed for next 4 to 6 hours while kept in plastic containers in the temperature control room (20 ± 2 °C). Samples for TG-DTA and XRD analysis were made as 3 × 13 × 300 mm prisms and compacted by vibrating on a compaction table. For compression tests, 50 × 100 mm cylindrical specimens were made and compacting of the material was performed 3 times both by rodding and by vibrating. After that, samples were sealed in the molds and stored in the temperature control room (20 ± 2 °C) until their demolding. Prismatic samples were demolded at the age of 3 days and then sealed again in wrapping foil and in an aluminum bag while cylindrical specimens were kept in the molds until the day of compression loading.

2.2 Compressive strength and elastic modulus

Hardened cement paste was subjected to a compression test at the age of 3, 7, 14 and 28 days. The

1 JCI member, Student, Graduate School of Environmental Studies, Nagoya University, Japan
2 Student, School of Engineering, Dep. of Environmental Engineering and Architecture, Nagoya Univ., Japan
3 JCI member, Professor, Graduate School of Environmental Studies, Nagoya University, Japan

Table 1 Properties of the cement

Density (g/cm^3)	Blaine value (cm^2/g)	Loss on ignition (%)	Chemical composition [%]										
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5
3.17	4 300 *	1.48	21.51	3.62	4.24	63.11	2.01	2.60	0.17	0.57	0.38	0.05	0.32

* value given by the producer

cylindrical specimens were demolded at the day of testing and immediately placed into an aluminum bag. The top of surface of each sample was polished by a grinding machine to obtain a flat face for loading. Polishing time to obtain a satisfactory surface was approximately 6 minutes but it differed for each sample. During polishing, a whole sample was subjected to water stream which was used for cooling of the material. Each sample was dried by a paper towel immediately after removing from the polishing machine and then placed again into the aluminum bag until the loading. Due to the polishing, the height of each sample was reduced and the final height varied from 95 mm to 97 mm.

The samples were compressed by a universal compressive machine. Firstly, an elastic modulus was measured by a compression meter which was attached to 5 cm long central part of the sample with two deflectometers having precision of 0.001 mm. Since elasticity is related to recoverable elastic energy of the material, the elastic modulus was calculated from the unloading part of the stress-strain curve. Approximately 5 % and 30 % of the compressive strength was taken as lower and upper limits for the calculation. After the specimen was compressed to obtain data for calculation of the elastic modulus, the compression meter was removed and the specimen was loaded for the second time until its ultimate compressive strength was reached. The loading speed was 0.3 MPa/s in both cases. The data reported in this paper represent an average value obtained on 3 specimens.

2.3 TG-DTA analysis

TG-DTA was performed on a sample of cement paste at ages of at 3, 7 and 14 days. Additionally, an analysis was carried out on dry cement powder. In order to stop the hydration process at the desired age, the samples were placed into a freezer and kept there until the analysis. Amount of the sample for the analysis was 20 mg (± 0.05 mg) and the initially solid cement paste was grinded to particles smaller than 100 μm under a protective atmosphere of nitrogen gas.

Analyzed samples were heated from the ambient temperature to 1000 °C with the rate of 10 °C/min by the TG-DTA analysis device. During the heating, the first peak at differentiated TG curve (DTG) appears due to release of evaporable water in temperature range from 100 °C to approximately 180°C. The final temperature of water evaporation varied based on its amount in the sample and the high final temperature was caused by the relatively high heating rate. Portlandite is decomposed around temperature range from 380 °C to 470 °C [15] and the mass reduction at this stage is caused by water vapor release. By integrating of the area of this peak, ignited mass can be obtained and the original mass of portlandite can be restored. Thermal decomposition of portlandite into calcium oxide and water and the quantification of the reaction in terms of molar mass (g/mol) are given as follows:

$$Ca(OH)_2 \xrightarrow{HEAT} CaO + H_2O \quad (1)$$

$$74 \longrightarrow 56 + 18 \quad (2)$$

Based on Eq. 2, it is possible to quantify the original mass of portlandite by multiplying the ignited mass of water by factor of 74/18 = 4.11.

In the later stage of DTG data, two carbonation peaks appear at ranges from 490 °C to 630 °C and from 720 °C to 920 °C [15] respectively. Those peaks are given by thermal decomposition of calcium carbonate into calcium oxide and associated release of carbon dioxide. Resulting data were normalized with respect to the final mass at the end of heating.

2.4 XRD analysis

The XRD analysis was performed at the age of 3,

Table 2 Characteristics used for phase calculation

Component name	Cement notation	Density (g/cm^3)	Molar mass (g/mol)	Water mass (%)
Amorphous	$C_{1.7}SH_{2.5}$	2.41	200.45	22.47
Periclase	M	3.58	40.30	-
Bassanite	$C\bar{s}H_{0.5}$	2.78	145.15	6.21
Gypsum	$C\bar{s}H_2$	2.32	172.17	20.93
Anhydrite	$C\bar{s}$	2.97	136.14	-
Calcite	$C\bar{c}$	2.71	100.09	-
Aluminate	C_3A	3.03	270.19	-
Ferrite	C_4AF	3.73	485.96	-
Belite	C_2S	3.28	172.23	-
Alite	C_3S	3.15	228.31	-
Portlandite	CH	2.26	74.09	24.31
Monocarbonate	$C_4A\bar{c}H_{11}$	2.17	568.45	34.86
Hemicarboaluminate	$C_4A\bar{c}_{0.5}H_{12}$	1.99	564.46	38.30
Ettringite	$C_6A\bar{s}H_{32}$	1.78	1094.98	52.65
Hydrogarnet	C_3AH_6	2.52	378.28	28.57
Water	H	1	18.02	100

7 and 14 days. The hydration process was stopped at the desired age by isopropanol. Firstly, hardened cement paste was crushed by a hammer into pieces smaller than 2 mm and immersed into isopropanol for 30 minutes. After the immersion, isopropanol was eliminated by a suction filtrations and the cement grains were immersed into isopropanol for another 6 hours and then isopropanol was eliminated in the same way for the second time. Once the hydration process was stopped, samples were dried in a lithium chloride controlled humidity chamber of 11% RH using circulated air flowing through a carbon dioxide absorbent. Prior to the analysis, the samples were grinded into powder. Then, 1 mg of the powder was mixed with 0.1 mg of corundum powder (α-Al_2O_3) used as an internal standard and isopropanol was added to the mixture. Dispersion of the resulting system was obtained by mixing it in a rotation mixer. Before the measurement, isopropanol was eliminated by suction filtration. An X-ray diffractometer were used under following conditions: Cu-KαX-ray source, 40 kV tube voltage, 40 mA tube current, $2\theta = 2 \sim 65°$ scanning range, 0.02° step width and 0.5°/min scanning speed.

Results of the X-ray diffraction measurements are shown at Fig. 4. Subsequently, the Rietveld analysis was performed to obtain the composition of the grounded cement paste. Following components were detected: corrundum (internal standard), amorphous phase considered entirely as C-S-H gel ($C_{1.7}SH_{2.5}$), periclase (M), bassanite ($C\overline{s}H_{0.5}$), gypsum ($C\overline{s}H_2$), anhydrite ($C\overline{s}$), calcite ($C\overline{c}$), aluminate (C_3A), ferrite (C_4AF), belite (C_2S), alite (C_3S), portlandite (CH), monocarbonate ($C_4A\overline{c}H_{11}$), hemicarboaluminate ($C_4A\overline{c}_{0.5}H_{12}$), ettringite ($C_6A\overline{s}H_{32}$) and hydrogarnet ($C_3AH_6$). Lastly, the mass of the internal standard was eliminated from the system.

3. RESULTS AND DISCUSSION

3.1 Compressive strength and elastic modulus

Compressive strength Fig. 1 as well as elastic modulus Fig. 3 obtained on cylindrical specimens have shown faster development as well as higher value at 28 days in case of 0.40 w/c ratio compare to 0.52 w/c ratio. This is consistent with general findings of mixture design of cement and concrete [5]. Also, the results suggest a possible future increase in the mentioned mechanical properties after the observed time period.

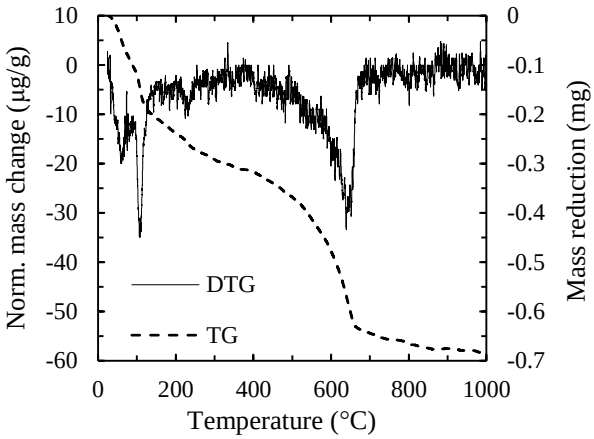

Fig. 2 TG-DTA of unhydrated cement

3.2 TG-DTA of unhydrated cement

A certain amount of calcium carbonate was obtained by analyzing unhydrated cement powder Fig. 2. This probably originates from air humidity penetrating into the cement package during shipping and storing, hydration of the clinker and subsequent reaction of the hydration products with carbon dioxide. This phenomenon was previously reported [13].

3.3 Phase composition

The phase composition Fig. 5 was obtained directly from XRD data and the Rietveld analysis [14]. The total amount of chemically bound water (CBW) was estimated from the chemical composition of every component based on the ratio of molar mass of water to the total molar mass of the component. Based on the w/c ratio, the initial unit mass of water used for sample preparation was calculated. At every age of the cement paste, the unit mass of capillary water was calculated by subtracting the difference in chemically bound water at a given age and the initially bound water from the mass of water used for sample preparation. By density of each phase, the mass of every phase was converted into its volume and normalized. Characteristics used for the calculation are listed Table 2 [9] - [11] and represents values at 20°C.The mass of chemically bound water and the mass of portlandite obtained from XRD data was confirmed through TG-DTA. The mass of chemically bound water was obtained from temperatures ranging from 105°C to 1000°C. The mass of portlandite was

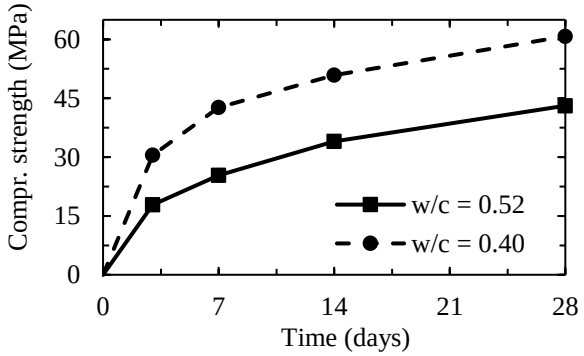

Fig. 1 Development of compressive strength

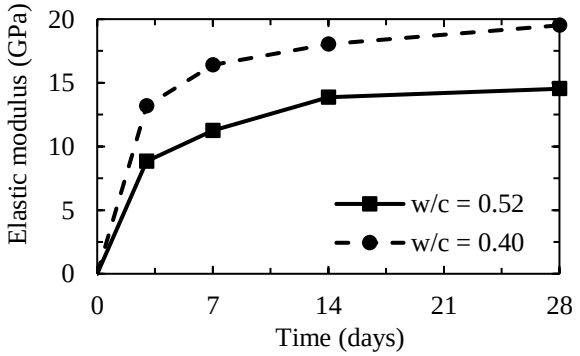

Fig. 2 Development of elastic modulus

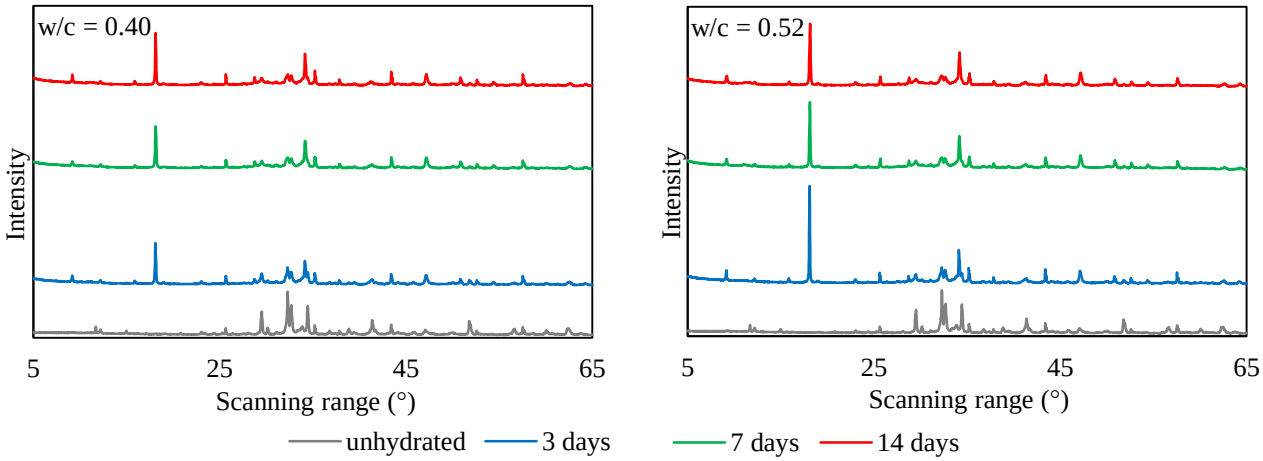

Fig. 4 Results of XRD analysis

calculated from the ingnated mass of water based on Eqs. 1 and 2. Comparison of those two methods shows a generally good agreement Fig. 6 and Fig. 7. An inaccuracy of this procedure arises from the fact that all amorphous phase was considered only as C-S-H while, in fact, also C-A-H and C-F-H phases with different amount of chemically bound water are presented in the system.

3.4 Degree of hydration

From the XRD results, volumetric content of clinker components, such as alite, belite, aluminate and ferrite, were obtained for every age and based on the initial composition, degree of hydration (DoH) was calculated by Eq. 3 and, moreover, an average degree of hydration was calculated.

$$\alpha = 1 - \left(\frac{V_{i,0}}{V_{i,t}}\right) \quad (3)$$

where,

α :degree of hydration

$V_{i,0}$:initial volumetric content of each clinker mineral

$V_{i,t}$:volumetric amount of the clinker at a given time

It can be observed from Fig 8 that the trend is similar, the average degree of hydration reaches almost 0.8 for both w/c ratios at the end of the observed period. The data showed a little difference in hydration of aluminate however, its amount in unhydrated cement powder is negligible Fig. 5.

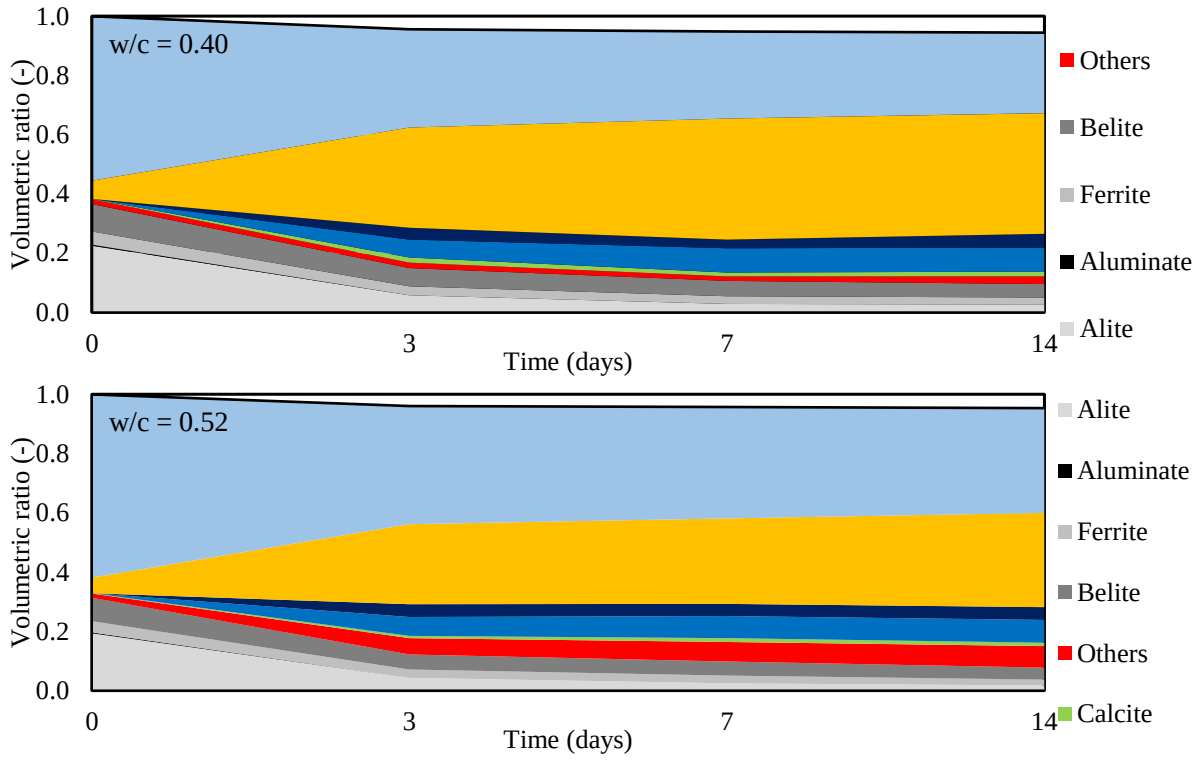

Fig. 5 Calculated phase composition

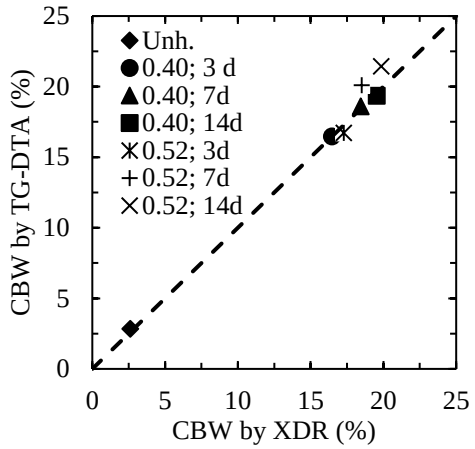

Fig. 6: Comparison of chemically bound water obtained by XRD-Rietveld analysis and by TG-DTA

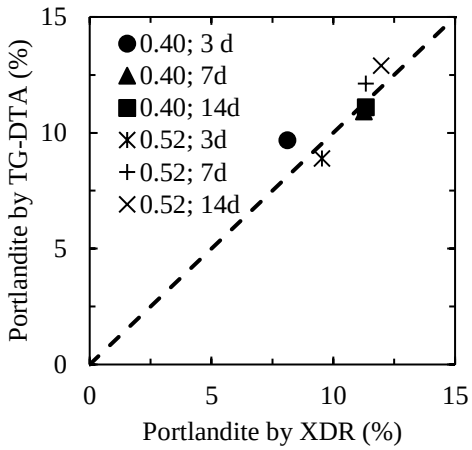

Fig. 7 Comparison of portlandite amount obtained by XRD-Rietveld analysis and by TG-DTA

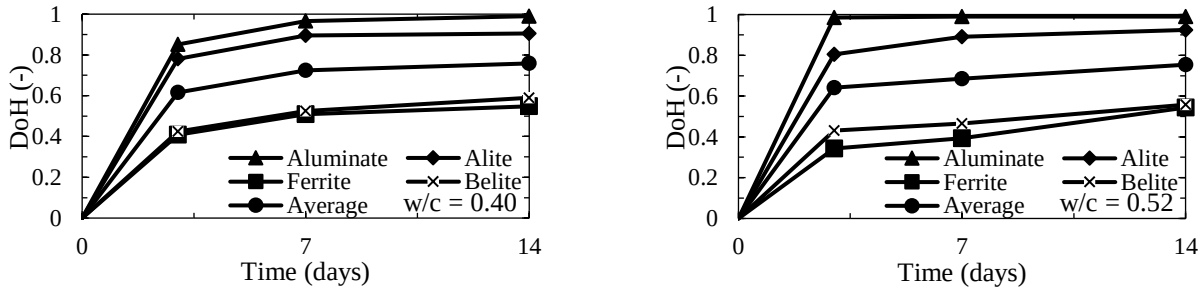

Fig. 8 Development of degree of hydration

3.4 Gel/space ratio

Based on the phase composition, gel/space ratio can be evaluated to predict mechanical properties of the material Eq. 4.

$$X = \frac{V_{gel}}{V_{gel} + V_{pore}} \quad (4)$$

where,

X :gel/space ratio (-)
V_{gel} :total gel volume (-)
V_{pore} :total pore volume

In this case, the total volume of gel was obtained as a sum of unit volumes of hydration products while a sum of unit volumes of capillary water and pores were taken as the total volume of pores. To fit the experimental results, the evaluation based on Power's research [2] was applied Eq. 5:

$$\sigma = \sigma_0 \cdot X^N \quad (5)$$

where,

σ :strength predicted (MPa)
σ_0 :material constant (MPa)
N :material constant (-)

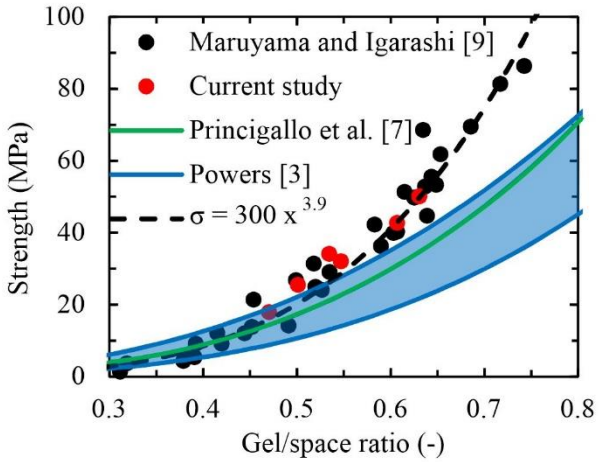

Fig. 9 Compressive strength as a function of gel/space ratio

The experimental result can be fit for values σ_0 = 300 MPa and N = 3.9 with a reasonable level of accuracy Fig. 9. This is consistent with results obtained by the same experimental procedure [9].

Powers [3] reported coefficient σ_0 ranging from 89.6 to 127.6 MPa and N from 2.44 to 3.0*8* for 5 different cements while the calculation of the gel/space ratio was based on the amount of non-evaporable water measured by the magnesium perchloride method. In case of drying of the samples by the dry ice method, resulting values of N increased about 12 % higher. Taplin [4] published his results of ultimate compressive load as a function of ratio of hydration products per gram of cement. Pichler et al. [8] post-processed his data and, since the trend of the function is not influenced by the experimental set-up nor if stress or load is measured, his N value ranging from 2.11 to 3.42 has the same nature as in the research done by Powers. To determine the amount of hydration products, Taplin stopped the hydration process by vacuum drying first then, to release evaporable water, the samples underwent heating up to 125 °C and, lastly, the samples were heated up to 540 °C. Then, the amount of hydration products were calculated from the ignited mass. Berger, Lawrence and Young [6] measured

strength of cement cylinders by the split cylinder test then D-dried the material and calculated the gel/space ratio from results of X-ray diffraction. The constants of their fit are σ_0 = 15.5 MPa while N = 3.0 is fixed. Principallo et al. [7] measured compressive strength on cubic samples and reported σ_0 = 138 MPa while, same as in the previous case, N = 3.0 is fixed.

Constant σ_0 depends on the experimental set-up for strength measurement therefore, the reported values differ significantly. On the other hand, the trend of the function given by N should be similar. However, the gel/space ratio depends on pore volume therefore, on the definition of pores, the experimental technique and the sample preparation method respectively. In our case, N value is larger which origins from the drying process and resulting density of C-S-H hydrates prior to the XRD analysis. Since some of the mentioned methods based on measuring of evaporable water have a rather larger impact on the microstructure [16], the obtained total pore volume increases. In contrast of a great significance of sample preparation techniques, based on the findings presented here, a phase composition can be calculated by the simplified approach from XRD-Rietveld data

The results obtained in this study indicates that the previously obtained relationship between gel/space ratio and compressive strength is universal and this curve is applicable to Portland cement produced in EU, while the sample treatment is in equilibrium to the vapor from saturated lithium chloride solution at room temperature.

4. CONCLUSION

Compressive strength and elastic modulus were measured on cylindrical specimens made from European-produced Portland cement while w/c ratios of 0.40 and 0.52 were used. The hydration process was evaluated based on XRD-Rietveld analysis and subsequently phase composition was calculated based on the amount of chemically bound water in each component and the original water to cement ratio. Based on the composition, the gel/space ratio was calculated and results were compared with a study published earlier. Following findings can be summarized:

(1) A phase composition can be obtain directly from XRD–Rietveld analysis. This was confirmed by comparison of calculated values of chemically bound water and portlandite with values directly obtained from TG-DTA analysis.

(2) The gel/space ratio hypothesis and the relationship for predicting of compressive strength of cement paste were confirmed.

(3) A certain level of carbonation was found in dry cement powder. This is a result of penetration of air humidity into the cement package.

ACKNOWLEDGEMENT

The authors greatly acknowledge the supports of Nagoya University and project COST TU1404 RRT+. A part of experiment was financially supported by a collaborative research project with Chubu Electric Power Co., Inc.

REFERENCES

[1] Powers, T. C., Brownyard, T. L., “Studies of the physical properties of hardened cement paste”, Part 1 – Part 9, ACI Journal, Vol. 43, 1947-1948

[2] Powers, T. C., “Structure and physical properties of hardened cement paste”, Journal of the American Ceramic Society, Vol. 41(1), 1958

[3] Powers, T. C., “Physical properties of cement paste“, Fourth international symposium on the chemistry of cement, Washington, D. C., 1960

[4] Taplin, J.H., “A method for following the hydration reaction in Portland cement paste”, Australian Journal of Applied Science, Vol. 10(3), 1959, pp. 329-345

[5] Abrams, D.A., “Design of concrete mixtures”, Bulletin 1 of Structural materials research laboratory, Lewis institute, Chicago, 1919

[6] Berger, R., Lawrence, F. and Young, J., “Studies on the hydration of tricalcium silicate pastes II. Strength development and fracture characteristics”, Cement and Concrete Research, Vol. 3(5), 1973, pp.497-508

[7] Principallo, A., Lura, P., van Breugel, K. and Levita, G., “Early development of properties in a cement paste: A numerical and experimental study”, Cement and Concrete Research, Vol. 33(7), 2003, pp.1013-1020

[8] Pichler, B., et al., “Effect of Gel–space Ratio and Microstructure on Strength of Hydrating Cementitious Materials: An Engineering Micromechanics Approach,” Cement and Concrete Research, Vol. 45, 2013, pp. 55-68

[9] Maruyama, I. and Igarashi, G., “Cement reaction and resultant physical properties of cement paste”, Journal of Advanced Concrete Technology, Vol. 12(6), 2014, pp. 200–213

[10] Balonis, M. and Glasser, F.P., “The density of cement phases”, Cement and Concrete Research, Vol. 39(9), 2009, pp. 733–739

[11] Taylor, H.F.W., “Cement chemistry. 2nd ed.”, Academic Press., 1990

[12] Singh, S.B., Munjal, P. and Thammishetti, N., “Role of water/cement ratio on strength development of cement mortar”, Journal of Building Engineering, Vol. 4, 2015, pp. 94–100

[13] Pane, I. and Hansen, W., “Investigation of blended cement hydration by isothermal calorimetry and thermal analysis,” Cement and Concrete Research, Vol. 35(6), 2005

[14] Matsushita, T. et al., “Effect of Curing Temperature and Water to Cement Ratio on Hydration of Cement Compounds”, Proc. of Int. Cong. on Chem. of Cem., 2007

[15] Scrivener, K., Snellings, R. and Lothenbach, B., “A practical guide to microstructural analysis of cementitious materials”, CRC Press, 2015, pp. 177-212

[16] Zhang, J. and Scherer, G., “Comparison of methods for arresting hydration of cement”, Cement and Concrete Research, Vol. 41(10), 2011, pp.1024-1036