- Technical Paper -

EVALUTION OF CHEMICALLY BOUND WATEWR OF WHITE CEMENT BY ^{1}H-NMR SOLID ECHO MEASUREMENT

Tatsuto HAJI*1, Ippei MARUYAMA*2, Takahiro OHKUBO*3, Ryo KURIHARA*1

ABSTRACT

Amount of chemically bound water, which is a result of cement hydration, is investigated with three measuring methods: thermal gravimetry analysis (TG), powder X-ray diffraction analysis with Rietveld quantification (QXRD) and 1H-NMR relaxometry. For the measurement procedures of TG and QXRD analysis, ^{1}H-NMR relaxometry results showed well-agreement with those obtained by QXRD. As a result, ^{1}H-NMR relaxometry using solid-echo (quadrature) would be alternative tool to quantify the chemically bound water in white cement paste systems.

Keywords: chemically bound water, TG, QXRD analysis, ^{1}H-NMR relaxometry, cement paste

1. INTRODUCTION

Concrete cracks on buildings shorten their lifetime. Cracks are caused by various factors, such as drying shrinkage [1], salt attack [2], and other environmental factors. Because cracks easily introduce the condition of rebar corrosion such as carbonization [3] or chlorite ion concentration [4]. In addition, drying of concrete itself has an impact on alternation of concrete strength and Young’s modulus [5], understanding of moisture in concrete is necessary for long-term use of buildings and infrastructure. For the first step of moisture analysis, the evaluation of chemically bound water is important.

In general, amount of chemically bound water in hardened cement paste has been evaluated by thermo-gravimetry (hereinafter, called TG) method, or simply the method using electric heat furnace with several step temperature increase and mass change measurement. Additionally, for example, powder X-ray diffraction with quantification Rietveld analysis (hereinafter, called QXRD), Fourier transform infrared spectra analysis (FT-IR) can be used. In this paper, ^{1}H-NMR relaxometry measurement, which is recently applied to cement chemistry [6-19] is focused. Then, the results were compared with the results of TG and QXRD.

The pretreatment of the measurement was also addressed. For example, TG measurement results were greatly affected by pre-condition of measurement. In case of moisture saturated surface dry block, slight evaporation has an impact on the measurement. In case of saturated hardened cement paste (hereinafter, called hcp), making powder has a difficulty. Therefore, for the reproducibility, some researcher use RH-conditioning before the measurement. It is also noteworthy that the amount of evaporable water has an influence of measurement results of chemically bound water using TG curve. To avoid such things, new method using slight freezing is proposed in this paper.

For the ^{1}H-NMR relaxometry measurement, it does not require any pretreatment. In addition, with ^{1}H-NMR relaxometry measurement, it takes a shorter time to measure than other two methods. It is nondestructive testing, which differs from others, so that change of state in-situ can be observed.

2. EXPERIMENT

2.1 Materials

In the experiment, white cement paste was used. ^{1}H-NMR relaxometry is affected by paramagnetic ions, for example, ferrite and manganese oxide in the cement clinker mineral (C_4AF, C: CaO, A: Al_2O_3, F: Fe_2O_3, notation in cement chemistry used here). Therefore, the white cement was applied in this study. Properties and characteristics of white cement (hereinafter, called W) are summarized in Table 1 and 2.

The water to cement ratios of the specimen were set as 0.40 and 0.55 (hereinafter, called W40 and W55 respectively). The paste was mixed in planetary centrifugal mixer at 1000 r/min for 1.5 min after the water was added to cement, and then the paste was mixed at 1000 r/min for a further 1.5 min after the paste was scraped from inside the mixer.

All the materials were stored in a thermostatic room at 20 ± 1 °C for 1 day prior to mixing. The mixing was performed at room temperature and the specimens were then immediately moved to a thermostatic room at 20 ± 1 °C. To minimize segregation, the paste was remixed every 30 min for 6 hours.

After the remix had been completed, the specimens were poured into plastic cylindrical container (for TG and QXRD) and glass cylindrical

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*1 Graduate student, Dept. of Environmental Engineering and Architecture, Nagoya Univ., JCI Student Member
*2 Prof. Graduate School of Environmental Engineering and Architecture, Nagoya Univ., Dr. Eng., JCI Member
*3 Assoc. Prof. Graduate School of Applied Chemistry and Biotechnology, Chiba Univ., Dr. Eng., JCI Member

Table 1 Chemical composition determined by XRD/Rietveld analysis*

Chemical composition	SiO_2	Al_2O	Fe_2O	CaO	MgO	SO_3	Na_2O	K_2O
mass %	22.68	4.50	0.19	65.07	1.19	2.75	0.06	0.07

Table 2 Mineral composition determined by XRD/Rietveld analysis*

Mineral composition	Alite	Belite	Aluminate phase	Periclase	Bassanite	Gypsm	Calcite
mass %	48.96±2.33	33.98±0.38	4.46±0.24	0.51±0.41	1.01±0.43	3.30±0.80	5.26±0.38

*Average of three measurements

container (for ^{1}H-NMR relaxometry). The specimens were sealed and cured in an aluminum package includes some moist cloths not to be dried, and they were placed in a thermostatic room at 20 ± 1 °C.

2.2 Measuring process

Summary of the experimental factors and the age at measuring are summarized in Table 3 and 4 respectively.

Amount of chemically bound water had been measured with TG and QXRD analysis on 1, 3, 7, 28 and 91 days after the paste was mixed. In case of ^{1}H-NMR relaxometry, chemically bound water was measured on the age shown in Table 4. The detailed procedures of each measurement are shown below.

2.2.1 TG

The specimens had been placed in freezer (-20 °C) to stop hydration on each age, 1, 3, 7, 28 and 91 days after the paste was mixed. Frozen specimens were crushed to powder, smaller than 150 µm, and the data of ignition loss and amount of de-carbonation of calcium carbonate phases, which exists in the original cement as shown in Table 2, were obtained. For the measurement, TG-DTA2010SA (Bruker AXS) was used. The powder specimen, weighs 20 ± 2 mg, was set on the TG machine. In measuring, the temperature was raised at 1 °C/min until 105 °C and was raised at 5 °C/min from 105 °C until 1000 °C. Under the nitrogen flow, the specimen was measured by dynamic mode, which was for keeping the temperature when the sample mass change was observed. The trigger of the sample mass change was less than 0.1 % of the sample mass per min. In addition, special temperature step was introduced to the measurement; the sample temperature had been kept at 105 ˚C for 7 hours. The reduction of mass from 500 °C to 800 °C was considered de-carbonation of calcium carbonate phases. The range of this trend was specified by DTA curve for each sample.

Fig. 1 shows TG curve of the hcp specimen, which is W55 at 7 days after the paste was mixing. The mass change from 20 °C to 105 °C and from 105 °C to 1000 °C were considered as the loss of evaporable water and chemically bound water respectively. To take account of de-carbonation of the specimen, amount of carbonate dioxide of calcium carbonate was deducted from the amount of chemically bound water. The area of this trend is shown in Fig. 1 as a down peak around 650 °C. To be compared with other methods, amount of chemically bound water per original anhydrous cement mass was calculated.

Table 3 Experiment factors

Parameter	Properties
Cement	White cement
Water to cement ratio	0.40, 0.55
Curing	Sealed (20 ± 1 °C)
Analysis	TG, QXRD, ^{1}H-NMR

Table 4 Age at measuring

Method	Age at measuring
TG, QXRD	1, 3, 7, 28, 91 (days)
^{1}H-NMR	1, 3, 6, 9, 12 (hours) 1, 1.5, 3, 7, 11, 14, 28, 91 (days)

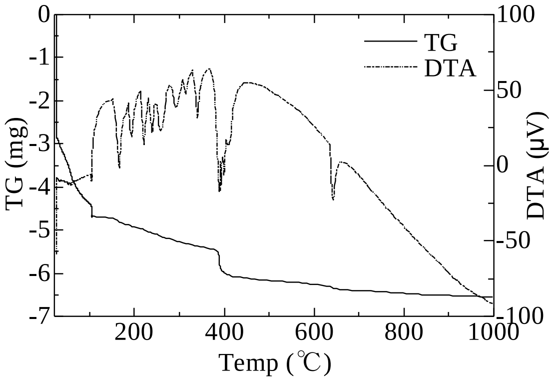


Fig 1 TG curve of the hcp (W55 7 days).

Equations are given as follows:

$$m = (m_{cbw} - m_{dc}) / m_{cem} \quad (1)$$

$$m_{cem} = m_{spc} - (m_{cbw} + m_{evp}) \quad (2)$$

where,

m	: amount of chemically bound water per 1 g anhydrous cement [g/g]
m_{cbw}	: amount of chemically bound water [mg]
m_{evp}	: amount of evaporable water [mg]
m_{spc}	: amount of specimen [mg]
m_{dc}	: amount of de-carbonation [mg]

2.2.2 QXRD analysis

The hcp specimens were analyzed by powder X-ray diffraction (XRD) (D8 advance, Bruker AXS) on 1, 3, 7, 28 and 91 days. All the hcp specimens had been submerged in isopropanol for 6 hours and had been dried under vacuum for several minutes with an aspirator. The specimens had been stored in a desiccator at 11% RH and 20 °C for 2 weeks. The specimens were put in a ball mill, and corundum powder (10 mass %) was added to the sample powder as a standard reference. The XRD conditions were as follows: tube voltage, 50 kV; tube current, 250 mA; scan range of 2θ, 5-65°; step width, 0.02°; scan speed, 2°/min. The software used for Rietveld analysis was TOPAS Ver. 4.0 (Bruker AXS). In the Rietveld analysis, the quantified phases were gypsum, bassanite, portlandite (CH), Hemi-carbonate (Hc), Hydrogarnet (Hg), Mono-carbonate (Mc), monosulfate (Ms), ettringite (Ett), periclase (M), as well as typical cement minerals, such as alite (C_3S), belite (C_2S), cubic-C_3A and orthorhombic-C_3A. Structural models for clinker minerals (alite, belite, cubic-C_3A and orthorhombic-C_3A) were taken from an NIST Technical Report [20]. Those for calcite, gypsum, bassanite, CH, Hc, Hg, Mc, Ms, Ett, M and corundum were taken from the ICSD database [21]. After the Rietveld analysis, the degrees of hydration of the clinker minerals and chemically bound water were calculated [22].

Amount of chemically bound water was calculated from amount of water in hydrates (ettringite, monosulfate, hydrogarnet, hemicarbonate, portlandite, and amorphous) at 105 °C to 1000 °C. The amount of water in a hydrate at 105 °C to 1000 °C can be calculated by subtraction of amount of the hydrate at 1000 °C from that of the hydrate at 105 °C. By QXRD analysis, the data of the specimen at 11 % RH can be gotten. The amount of water molecules as chemically bound water at sealed condition is back calculated by the result of phase composition at 11 % RH. Once phases at 11 % RH was obtained, and then each hydrates were converted unhydrated conditions, and chemically bound water and evaporable water at sealed condition were obtained. Table 5, which is basis for this back-calculation, shows each molecular weight of considered phases at 11 % RH, 105 °C and 1000 °C. The amount of chemically bound water with QXRD analysis was calculated on each age.

With regards to C-S-H, Ca/Si composition is calculated by mass balance of clinker minerals and detected crystal phases. For 11% RH condition, $H_2O/(Al + Si)$ is considered as a fitting parameter.

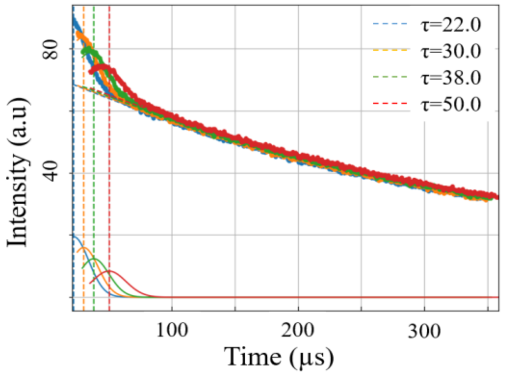
2.2.3 ^{1}H-NMR relaxometry

^{1}H-NMR measurements were conducted using a Bruker minispec equipped with a digital filter and a φ 10 mm probe. The magnet provided a resonant frequency of 20 MHz (0.47 T) for protons. The π/2 pulse length was 2.4 μs, which was calibrated on a solid cement sample.

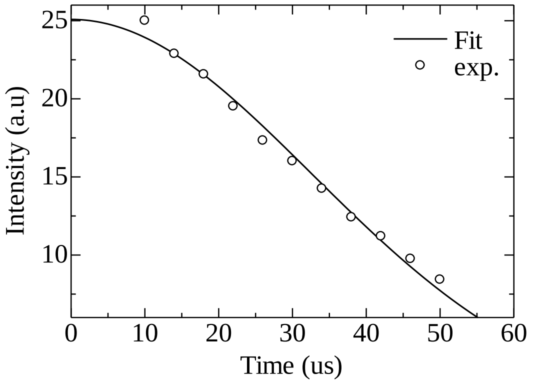
Relaxation delay was 1 s. The quantification of chemically bounded water was carried out following previous study by Muller et al. [10]: solid-echo (quadrature) decay signal was acquired and analyzed. The solid echo signal can be expressed by two components: (i) a rapid decay component arising from magnetic dipole-dipole (DD) interaction in solid phases and (ii) a slow decay component resulting from averaged DD interaction by molecular motion attributing to liquid-like water. The rapid decay due to DD interaction causes Gaussian line shape centered at an echo time (τ) with relaxation time $T_{2,\,solid}$ (order of μs). On the other hand, the slow decay results from liquid-like water yields exponential shape with $T_{2,\,liquid}$ (order of ms) from the first pulse. Hence, the detected signal intensity: $I(\tau, t)$ can be fitted to summation of two functions [23].

Table 5 Molecular weight of hydrates.

Name of hydrate	15%RH [g/mol]	105 °C [g/mol]	1000 °C [g/mol]
Ett	1255.10	894.79	678.61
Ms	622.51	550.45	406.33
Mc	586.46	514.40	326.27
Hc	573.46	501.40	326.27
Hg	378.28	378.28	270.19
C-S-H	200.45	182.43	155.41
C_4AH_{13}	560.46	452.37	326.27
CH	74.09	74.09	56.07



(a) Two component fitting gauss and solid exponential (line) and experimental decay data (dotted line).



(b) Back extrapolation of $I_S(\tau)$ to τ =0.

Fig. 2 An example of analysis for solid echo data with variable τ (W55 7 days).

$$I(\tau,t) = I_s(\tau)exp\left(-\frac{(t-\tau)^2}{(T_{2,solid})^2}\right) + I_l(\tau)exp\left(-\frac{(t+\tau)}{T_{2,liquid}}\right) \quad (3)$$

where,

I_s, I_l : contribution from solid and liquid-like water, which is directly related to molar fraction of solid and liquid-like water.

Decay signals were acquired for τ from 5 to 25 μs in 2 μs intervals, then signals were decomposed into Gaussian (solid) and exponential (liquid) parts according to Eq.(3). Relaxation artifact should be considered for infinite echo time. Therefore, I_s as a function of τ was back extrapolated to τ=0, and the accurate intensity from solid-like water was obtained.

As an example, the fitting results of $I(\tau, t)$ and back extrapolation of W55 at 7 days were shown in Fig. 2. Two components were well resolved for all decay data with different τ. It should be noted that exponential decay attributed to liquid-like water was nearly constant due to long $T_{2,\ liquid}$. Good extrapolation to τ=0 was also confirmed for all data. Ratio of amount of total water to that of chemically bound water is obtained by I_s and I_l at τ = 0. The chemically bound water per 1 g of anhydrous cement can be calculated by multiplying the ratio and water to cement ratio.

3. RESULTS AND DISCUSSION

3.1 QXRD analysis

The hydration process of cement pastes was evaluated by QXRD analysis. The obtained development of phase composition of W55 and W40 is summarized in Fig. 3.

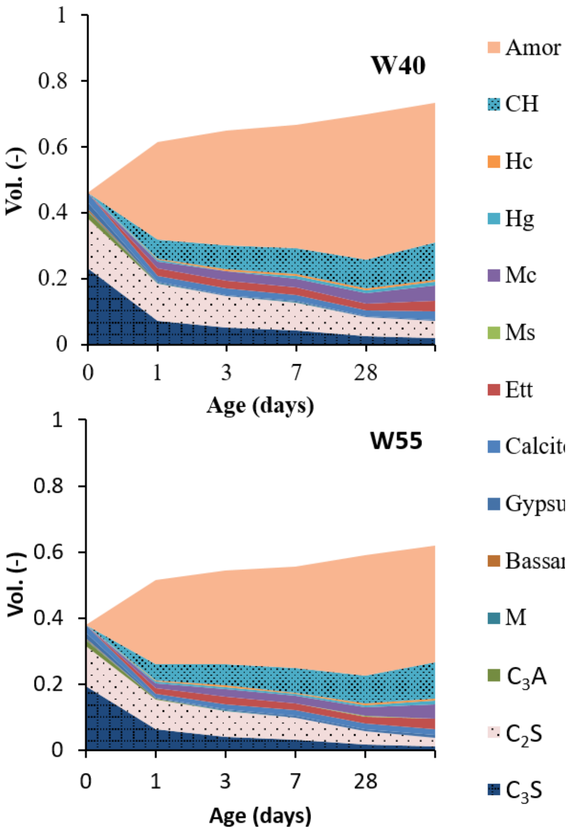


Fig 3 Phase composition of white cement.

3.2 Chemically bound water

Fig. 4 shows comparison of change in the amount of chemically bound water calculated by TG, QXRD analysis and ^{1}H-NMR relaxometry. As shown in Fig. 4, the amount of chemically bound water increases as the specimen getting matured regardless of the methods. This trend can be seen regardless of water to cement ratio of the specimen.

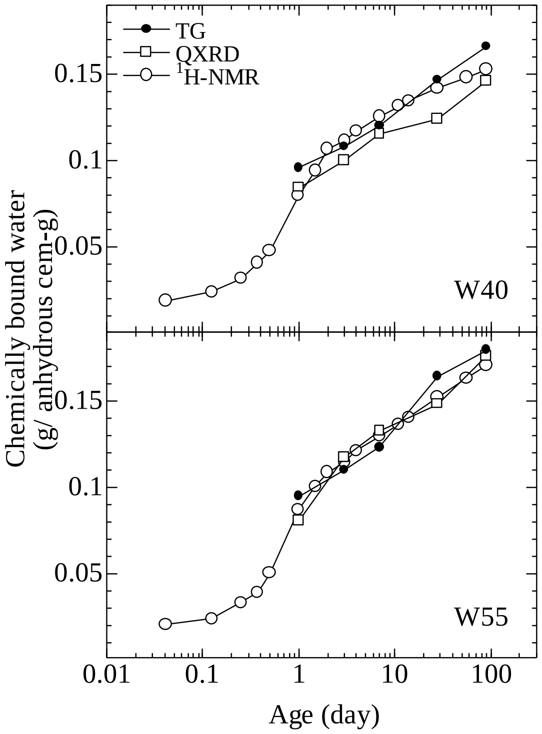


Fig 4 Amount of chemically bound water evaluated by TG, QXRD and ^{1}H-NMR relaxometry.

In early age, especially 1 or 3 days of curing, the amount of chemically bound water was similar regardless water to cement ratio. Although, the specimen of W55, after 28 days of curing, had much amount of chemically bound water than the specimen of W40.

Before 28 days of curing, the amount of chemically bound water with TG is almost identical to the data obtained by the other methods. However, it showed discrepancy when the sample is matured.

In case of the W55 specimen, the amount of chemically bound water by ^{1}H-NMR relaxometry is identical to that by QXRD with a H_2O/Si fitting parameter of 0.5. The obtained results were not consistent to the previous results. Muller et al. insists that the chemically bound water detected by solid echo pulse sequence is the crystal water molecules from crystalline cement hydrates such as portlandite, ettringite and monosulphate [10]. On the other hand, in our case, the total water detected by solid echo cannot explain the value calculated by such waters. The water relating to amorphous phase should be included to explain. In addition, the constant ratio of H_2O/Si is validated in hydrating process and different water to cement ratio cases.

By considering these results, there exist the water molecules in between calcium silicate layers of calcium silicate hydrates (C-S-H) in cement paste, and they does not diffuse / interconnected with gel/capillary water, and it shows Gaussian decay. In case of tobermorite model, above Ca/Si ratio of 1.5 cannot explain OH-group. Only water molecules in interlayer space as a part of crystal structure exist. In this case, based on Richardson's results [24], when the Ca/Si is 1.5, H2O/Si=1.26. Although the obtained number is less than these, it means that only about one water molecules is associated with two silicate atom. It means that only the water molecules located vicinity of silicate dimers shows Gaussian decay.

It is also possible to explain by using jennite ($Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$) model. In this case OH group exist which is associated with Ca atoms. The H_2O/Si is apparently 0.5, which can explain the obtained number. However, there remains the question why such a constant value is obtained. The fundamental background concept of water molecules associated with calcium atoms is well consisted with Gartner-Maruyama-Chen's C-S-H model [25].

4. CONCLUSIONS

In the present study, the amount of chemically bound water, which can be measured by thermo-gravimetric measurement, powder X-ray diffraction with quantification Rietveld analysis and ^{1}H-NMR relaxometry, was investigated. Based on the experimental results, the following conclusions are derived;

(1) As the sealed hardened cement paste specimen was cured longer, the amount of chemically bound water increased. Moreover, the amount of chemically bound water in hardened cement paste with water to cement ratio of 0.55 was larger than those of cement paste with water to cement ratio of 0.40 in matured state. This trend was confirmed by any measuring methods.

(2) There is different trend of the amount of chemically bound water measured by TG comparing with the other two methods especially after 28 days of material age. However, there is similar trend regardless of water to cement ratio of the specimen.

(3) Measured data by QXRD, in which H_2O/Si of C-S-H is assumed to be 0.5, and ^{1}H-NMR relaxometry were agreed in case of hardened cement paste with water to cement ratio of 0.55. In case of white Portland cement system, ^{1}H-NMR relaxometry has a high potential for the evaluation of chemically bound water because it takes shorter time than other methods and the data with ^{1}H-NMR relaxometry is similar trend to the data with QXRD. The obtained results contradicted with previously reported data by Muller et al. Based on the consisted measured data in the present study, the isolated H_2O or OH in amorphous phase, which shows Gaussian decay.

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