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Dielectric study on molecular dynamics in cement hydration

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Dynamics of free water in cement have not been studied enough, although it should be important to understand the mechanism of the consolidation process. The water/cement (W/C) ratio and curing time dependences of dynamical structure of free water were bound by time domain reflectometry measurements as follows; (1)Lower W/C ratio brought about larger relaxation time τ and smaller Cole-Cole exponent parameter β values. (2)Amount of free water decreased during the hydration reaction for various W/C ratios. (3)Higher water/cement ratio offered more amount of water in C-S-H gel. (4)The curing rate became sluggish with increasing W/C ratio. These results of free water behaviors observed in the cement hydration process are also useful to consider possible new evaluation systems for the qualities of cement paste, mortal, concrete, and so on.
Key words: free water, cement paste, time domain reflectmetry, water/cement ratio, curing time

1. INTRODUCTION

Cement and water mixtures gradually are hardened through the spontaneous hydration process; namely gel-like matrix of calcium silicate hydrate (C-S-H) interpenetrates the region between the adjacent cement grains [1, 2]. The major component of Ordinary Portland Cement (OPC) is tricalcium silicate $Ca_3SiO_5(C_3S)$, which is often used as a model of cement hydration particularly during the first few days of cure. The hydration reaction for mature C_3S paste is represented as [3]

$$Ca_3SiO_5 + (1.3+x)H_2O \rightarrow (CaO)_{1.7} - Si_2O - (H_2O)_x + 1.3Ca(OH)_2. \quad (1)$$

The static structure of C-S-H gel has been studied by x-ray analysis [1], transmission electron microscopy [4, 5], and nuclear magnetic resonance [6]. Dynamic structure of the hydration water (we call it "structured water") has been also studied by dielectric spectroscopy to understand the mechanism of the consolidation process of concrete [7, 8]. However, dynamics of free water have not been extensively studied, even if it seems to be very important to explain the mechanism.

Microwave dielectric measurement is one of the most effective methods to detect dynamics of water molecules. The relaxation process due to reorientation of water is also observed in pure water around 18 GHz at 25℃ [9]. In general, the relaxation process due to free water in aqueous mixtures is also observed by dielectric measurements, for example, via a time domain reflectometry (TDR) method [10-13] for aqueous solutions of polymers [14-17], aqueous gels [18], emulsions [19], and tissues in vivo and in vitro [20,21], and so on. The relaxation time, τ, the relaxation strength, $\Delta\varepsilon$, and the Cole-Cole parameter, β, for free water are reported for 20% bovine serum albumin solution at 25℃ as $\tau = 10$ ps, $\Delta\varepsilon = 46.7$, and $\beta = 0.99$, respectively [22], and these values depend on the concentration.

Recently, TDR measurements were performed for the hydration process of Portland cement paste, and a relaxation process due to free water was found around 10 GHz at 25℃ [8, 23]. This relaxation process rapidly decreased and another process due to structured water in calcium silicate hydrate (C-S-H) appeared around 100 MHz during the first three days. It was reasonably concluded that free water transformed to structured water during the hydration process. Furthermore, the relaxation process due to structured water continues to move to the lower frequency through the curing process. This characteristic feature is different from that of "bound water" suggested for proteins. This is a reason why we call the hydration water in the cement paste "structure water". The curing process should be observed more precisely and discussed more with the hydration mechanism.

In this work, we performed dielectric measurements for cement paste in the wide frequency range on the curing process in order to clarify the dynamical behaviors of free water. We also analyzed heterogeneous hydration structures of cement, and discussed possibility of a new method of non- or less-destructive test by the TDR system.

2. EXPERIMENTAL

2.1. Materials

Portland cement was provided from Chichibu-Onoda Cement Co. (Tokyo). Distilled and deionized water with an electric conductivity lower than 18.3 μS/cm was prepared by ultra pure water products (Millipore, MILLI-Q Lab). Milli-Q water was added to the cement. We prepared cement paste samples with various water/cement ratios (W/C) between 0.40, and 0.70 g/g.

2.2. Dielectric measurements

Complex permittivities of the cement paste samples with W/C of 0.40, 0.50, 0.60 and 0.70 were measured by TDR in the frequency range between 750MHz and 20 GHz. Temperature was controlled by an

temperature-controlled bath with a digital multi-meter during isothermal cure at 25.0℃.

A block diagram of the TDR system is shown in Fig.1. The reflected pulse from the sample was obtained in the a time domain at the sampling head (HP54121A, Hewlett-Packard) and digitized by a digitizing oscilloscope mainframe (HP54121B, Hewlett-Packard). An incident pulse with a rise time of 35 ps is generated by a pulse generator and passes through a 50 ohm coaxial line. The pulse is reflected from a sample cell at the terminal of the semi-rigid coaxial line, and detected by the sampling head. Complex permittivity values are obtained from the analysis including Fourier Transform. Details on the procedures of the dielectric relaxation measurements were reported in the previous paper [7].

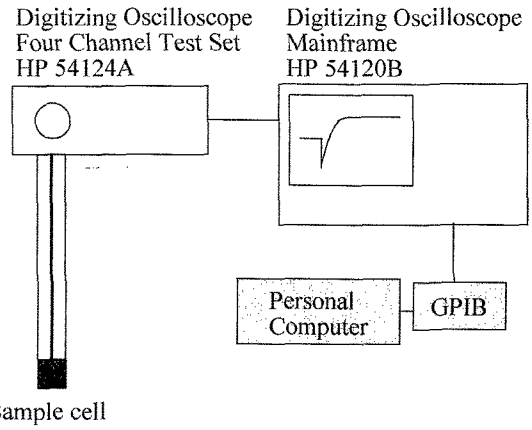

Fig. 1. Schematic diagram of TDR measuring system.

3. RESULTS AND DISCUSSION

3.1. Curing time dependences of dynamics of free water

Figure 2 shows dielectric dispersion and absorption for the cement paste at various curing times during the initial 20 hours at 25.0℃. The solid lines are the dielectric dispersion and absorption for pure water. The relaxation process with loss maximum frequency above 10 GHz is due to the orientation of free water molecules. The relaxation strength for free water observed in the higher frequency region decreased with the hydration.

3-2. water/cement ratio relaxation process of free water

Figure 3 shows dielectric dispersion and absorption for a cement paste with W/C=0.70 in 5 hours after mixing at 25.0℃. The curves were well described by one dielectric relaxation process and a contribution from dc conductivity. The complex permittivity, $\varepsilon^*(\omega)$, thus obtained for the cement paste was described as

$$\varepsilon^*(\omega)-\varepsilon_\infty = \frac{\Delta\varepsilon}{\left\{1+(j\omega\tau)^\beta\right\}}+\frac{\sigma}{j\varepsilon_0\omega} \quad (2)$$

where ε_∞ is the limiting dielectric constant at high frequency, j is the imaginary unit, σ is dc conductivity, ε_∞ is the permittivity of vacuum, β is the shape parameter $0<\beta\leq 1$ for symmetric broadening.

W/C ratio dependence of the relaxation time τ and the Cole-Cole exponent β obtained in 5 hours often mixing for-hydrated cement are shown in Fig. 4. In hydrated cement, τ increases and β broadens with decreasing W/C ratio. These results mean that the smaller fraction of free water is restricted by cement hydration. These properties of restricted water have been commonly observed by dielectric spectroscopy for various aqueous mixtures [14-17]. Therefore free water in cement paste shows similar characteristic feature of restricted water in various aqueous mixtures, at least, in initial hydration process.

The dielectric dispersion and absorption change with the curing time as shown in Fig. 2. Figure 5 shows the curing time dependence of the relaxation strength $\Delta\varepsilon$ and dc conductivity σ_{dc} for the cement paste with various W/C ratios. Down-arrow and up-arrow indicate the beginning and the end of hydration. The relaxation strength $\Delta\varepsilon$ corresponding to the amount of free water decreased with curing time especially for the cement paste samples with W/C of 0.40 and 0.50. This phenomenon is involved in the change in the concentration of cement during the measurement and the high viscosity for the samples with smaller W/C values. The relaxation strength $\Delta\varepsilon$ did not decrease before beginning of the hydration. This result is explained by the theory as the induction or dormant period [24]. When the early hardening began, the relaxation strength $\Delta\varepsilon$ decreases in the hydration process. This result also follows the theory for early hardening [24]. The amount of free water abruptly decreased with hydration for each W/C ratio. Furthermore, σ_{dc} values for the cements with higher W/C ratios were larger than those with lower W/C ratios, and decreased simultaneously with the hydration process.

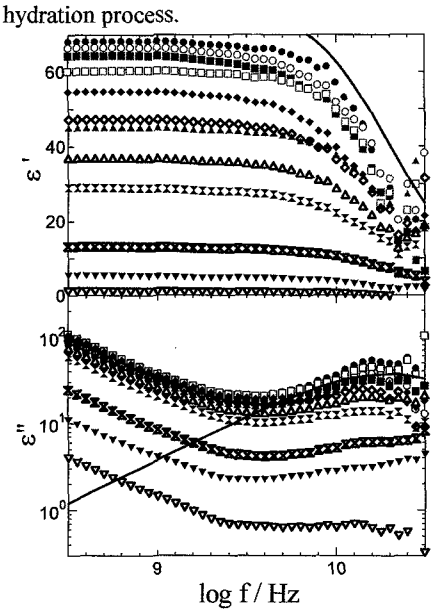

Fig. 2. Dielectric dispersion and adsorption of cement paste with water/cement = 0.70 at various curing times from 0 min up to 20 hours at 25.0℃.

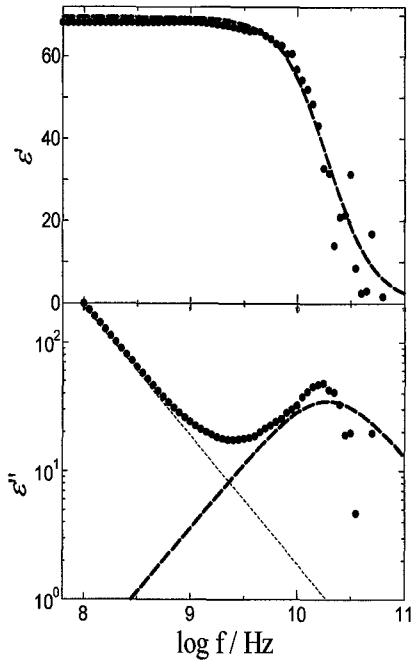

Fig.3 Dielectric dispersion and absorption for OPC of water/cement at 5 hours after mixing. A dash line is free water relaxation $\Delta\varepsilon$. Dot line is dc conductivity σ_{dc}.

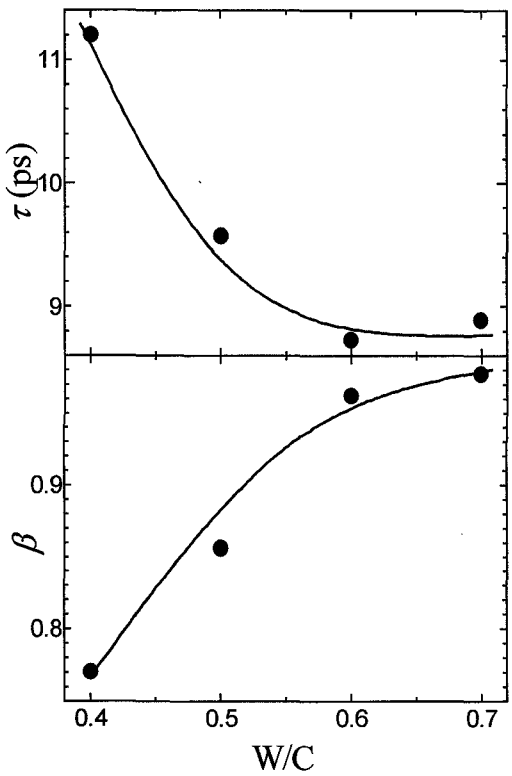

Fig. 4 Plots of the relaxation time τ and the Cole-Cole exponent β as a function of water/cement ratio.

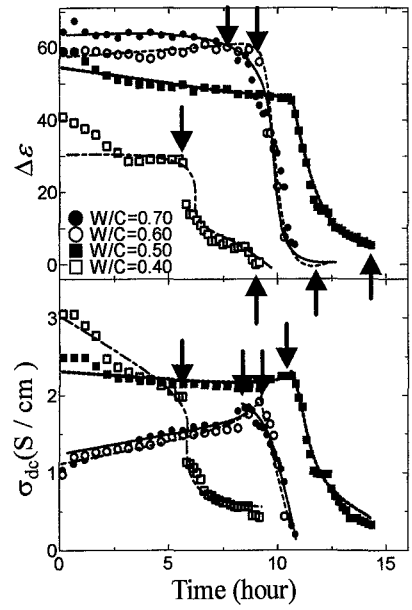

Fig. 5. Plots of relaxation strength Δε and conductivity the σ_{dc} as a function of the curing time for cement paste with various water/cement. Down-arrow and up-arrow indicate the beginning and the end of hydration.

The amount of water held by C-S-H gel can be expressed by the decrease in the relaxation strength $\Delta\varepsilon$ for free water, because the total amount of water in the sample is always kept by a sealed vial container. The change in the relaxation strength, $\Delta\varepsilon_{Start\text{-}End}$, is defined as a difference between the average of the relaxation strength Δε before the hydration and that estimated at the end of the hydration process $\Delta\varepsilon$. Figure 6 shows the W/C ratio dependence of the $\Delta\varepsilon_{Start\text{-}End}$ values. This result indicates that the cement paste with higher W/C ratio absorbs larger amount of water in the C-S-H gel.

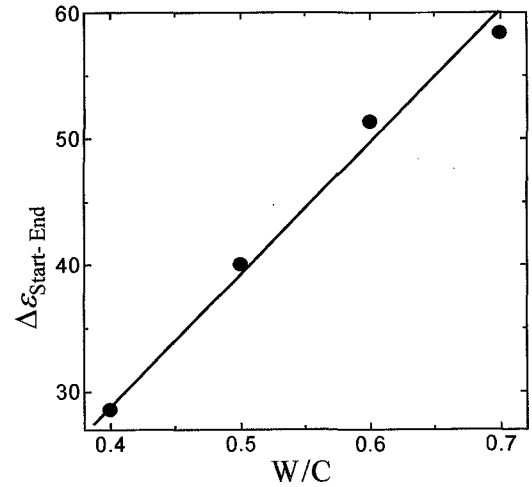

Fig. 6 water/cement ratio dependency of the change in the relaxation strength free water during the hydration.

The curing rate was considered from the curing time dependence. Δt, is defined the time at which the change in the relaxation strength is achieved 63 %. The value 63 % corresponds to the characteristic time constant of exponential decay behavior. Fig.7 shows the W/C ratio dependence of the time Δt obtained from Fig.5. The Δt

values decrease with decreasing W/C ratio. This result also indicates that higher W/C ratio brings the larger value of Δt.

Researches treating the cement hydration mechanism of free water suggest an advantage in understanding structures and properties like the crushing strength of C-S-H gel. Especially the amount of water in the C-S-H gel and curing time obtained in the present work are important to consider not only the fundamental science but also the possibility for new evaluation systems for the qualities of cement paste, mortal, concrete and so on.

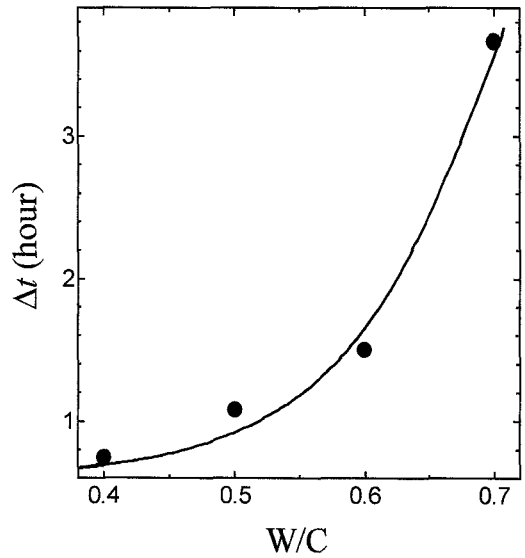

Fig. 7. Curing rate magnitude of relaxation strength 63% to water/cement ratio

4. CONCLUSION

Dielectric dispersion and absorption were observed by TDR measurements for cement paste samples with various W/C ratios. The relaxation process due to free water clearly depends on the curing time and W/C ratio. The W/C ratio and curing time dependencies thus obtained here suggest that free water shows similar behaviors with slow dynamics of water included in various aqueous systems. These results of free water behaviors observed in the cement hydration process are also useful to consider possible new evaluation systems for the qualities of cement paste, mortal, concrete, and so on.

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