

Microstructure and strength change of hardened cement paste under drying process

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ABSTRACT

Water vapor sorption isotherms, nitrogen sorption isotherms, and bending strength of cement paste cured with different relative humidity for 1 year are measured. Effect of drying on microstructure has two ways. One is nano-scale effect, in which nano-scale pore among globules is collapsed due to capillary tension or solution and re-precipitation cycle of C-S-H. The other one is atomic-scale effect, in which water adsorption sites are reduced due to drying by changing of other than Si network. From such effect, cement paste shows different nature of microstructure according to thermodynamic conditions, and resultantly, the physical properties are altered.

Keywords. White cement paste, Drying process, Shrinkage, Bending strength

1. INTRODUCTION

Among hydrates from cement minerals, calcium silicate hydrate (C-S-H), has been intensively studied from many aspects. Recently, not only volume change behavior of cement paste due to water content change, but also inconsistent experimental results of properties of C-S-H and hardened cement paste (hcp) have changed the way of thinking of researchers. It is emphasized that C-S-H is now considered as a gel-like or colloidal system whose nature is strongly related to surrounding water molecules (Scherer 1999, Jennings 2000 and 2008, Thomas and Jennings 2006, Setzer 2007), while it was previously considered as a rigid porous material in earlier studies.

There are plenty of experimental data of C-S-H or cement paste, but still the effect of drying, especially regarding first desorption process, is not fully-understood. Based on this background, sorption experiment with different probes such as water vapour and nitrogen is applied to understanding nano-scale and atomic-scale change under different relative humidity condition. At the same time, physical properties of cement paste are tested. And Relationships of such results are discussed.

2. EXPERIMENT, RESULTS, AND DISCUSSIONS

2.1 Experimental procedure

Sample of cement paste. White cement provided by Taiheiyo cement company was used. Water cement ratio was 0.55, and 10l of paste was mixed by in a Hobart mixer with of 20l capacity for 3 minutes after introducing adding water and for another 3 minutes after scraping the adhered paste from inside of the mixer. All the materials were stored in a thermostatic room at $20 \pm 1^\circ\text{C}$ one day prior to mixing. Mixing was performed at room temperature and the specimens were then immediately moved to a thermostatic room. To minimize segregation, it was remixed until the age of six hours. A batch of paste was poured into a tub, and it was remixed every 30 min, and was then cast in molds. The specimens were placed in a thermostatic chamber at a temperature of $20 \pm 1^\circ\text{C}$, and were demolded after 4 days and cured under lime-saturated water until the curing under different RH conditions was commenced at 180 -days of age. Specimen size was generally 3 x 22 x 300 mm. This size was selected by for efficiency of the drying process (Maruyama 2010). At the same time, specimens with the size of ϕ 50 x 100 mm were also made by using light- weight steel moulds. These specimens were cured and stored under lime-saturated water even after 180-days of age.

Curing condition. The specimens in this experiment were stored in a controlled-humidity chamber for 12 months. The relative humidity in the chamber was controlled by a sodium hydrate solution. The targeted relative humidities were 98, 95, 90, 80, 70, 60, 50, 40, 30 20 and 11% at $20 \pm 1^\circ\text{C}$. The resulting relative humidities were monitored with a humidity sensor with a precision of 1.8% RH (Sensirion SHT75), and were controlled within 2% RH after the first 28 days of curing. The major reason of for using sodium hydrate was to avoid carbonation of hcp.

Condition of samples. The degree of hydration of each cement mineral is evaluated by X-ray powder diffraction and Reitveld analysis. The precise procedure is described elsewhere (Maruyama and Igarashi 2011). 3 times of measurement for each condition were performed and average value is evaluated.

Water vapour sorption measurement. Water vapor sorption measurements were conducted by the volume method. Quantachrome Hydrosorb1000 was used. Samples were ground by a ball mill, and powder with diameters ranging from 25 to 75 micrometers was used for this analysis. Sample pretreatment was as follows. They were vacuumed by a vacuum pump (Minimum pressure 6.7×10^{-2} Pa, and observed maximum value 50 Pa) and heated to 105°C by a Mantle heater for 30 min. A sample of about 20mg was used for each measurement and the measurement conditions were 20°C , pressure tolerance of 0.05mmHg, and time in tolerance of 120 sec. Measurement points in the adsorption branch were 5%RH intervals up to 95%RH, ending at 98%RH. Measurement points in the desorption branch were the same as those in the adsorption branch. The water vapour BET surface area (hereafter $S_{\text{H}_2\text{O}}$) of the adsorption branch was calculated using BET theory with a water molecule section value of 0.114 nm^2 (Mikhail 1966).

Nitrogen sorption measurement. The same size samples as for water vapor sorption measurements were used for nitrogen sorption measurement. The samples were after 9-month curing. Pretreatment procedures were also the same as those of water vapor sorption measurements. The used facility was Micrometrics TriStar II 3020.

Bending test. 3-point bending test with 60 mm-span (shear-span is 30 mm) is applied to the specimen with 3 x 13 x 300 mm. Each curing condition has 5 data and average of them is evaluated.

2.2 Results and discussions

Figure 1 represents the results of XRD/Rietveld analysis, and based on this figure, degree of hydration is not different among each sample with different curing condition, while small increase of degree of hydration of C_2S is confirmed in a range from 70%RH to 95%RH.

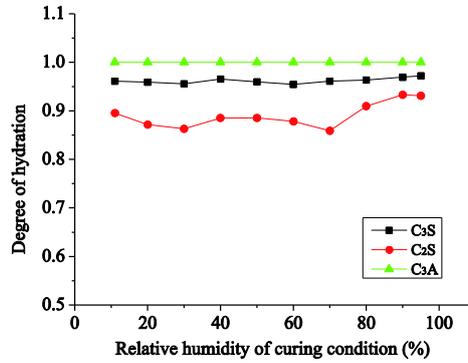


Figure 1. Degree of hydration of each cement minerals in cement paste cured under different relative humidity for 1 year.

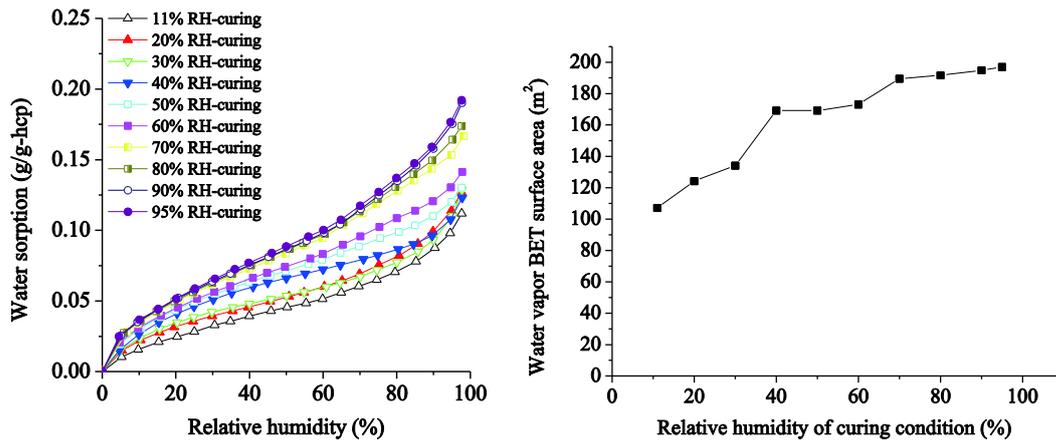


Figure 2. Water vapor sorption isotherm of cement paste cured under different relative humidity for 1 year (left) and BET surface area of cement paste (right).

Figure 2 shows the results of water vapor sorption isotherms of cement paste cured under different relative humidities for 1 year, and calculated BET surface area (S_{H_2O}). As it is confirmed that samples cured above 70%RH shows the same S_{H_2O} and the same trend of isotherms under 70%RH. The drying process affects on the sorption amount between 60%RH and 95%RH (hereafter, dW_{98-60}). And S_{H_2O} is decreased as the curing condition of relative humidity is decreased, especially in the range from 40%RH to 11%RH. Figure 3 shows the results of nitrogen isotherms and BET surface area (S_{N_2}). It is well known that nitrogen does not have a polarity, therefore, the accessible pore is limited and different from those by water vapor. Resultantly, the values of S_{N_2} is much smaller than those of S_{H_2O} . Similar results of S_{N_2} have been reported by Hant (1966), Litvan and Myers (1983), and Parrot et al. (1980).

It is considered that N_2 accessible pore is connecting the surface of the sample powder and has nano-meter size, while water vapor can penetrate the interlayer space of C-S-H, and

penetration of vapor will not be disturbed by the presence of globule (Jennings 2000, 2008). Based on this knowledge, the consistency of S_{N_2} and dW_{98-60} at the range from 60%RH to 98%RH (shown in Figure 4) represents that drying process collapses or eliminates the Large Gel Pore (LGP) which is located between globules. This can be due to capillary tension of pore solution (Parrot et al. 1980) or solution - re-precipitation cycle of C-S-H. Because the pore solution stay in narrower or smaller pore, therefore, the liquid phase is generally located in the cement hydrates around the unreacted cement core. If the solution and re-precipitation of C-S-H takes place, the re-precipitated area should be near the unreacted cement core. Therefore, for a long time, packing of globule is generated.

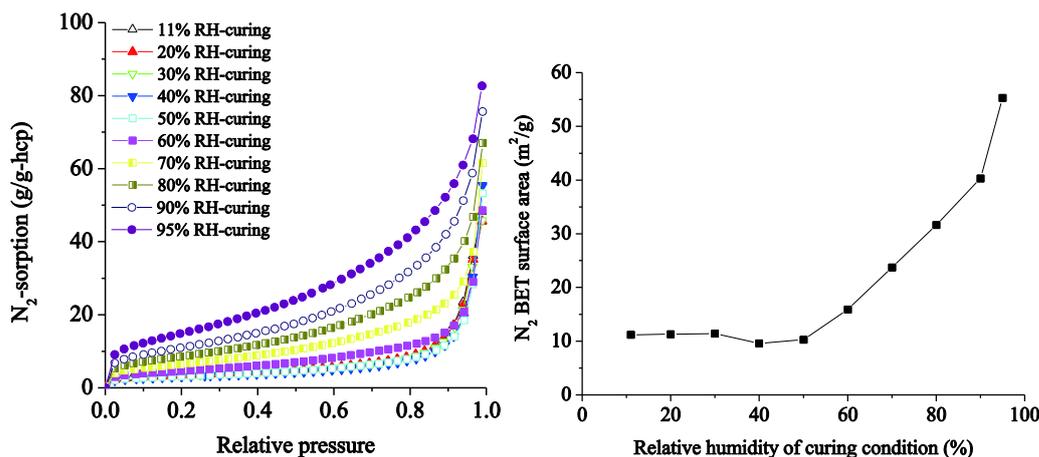


Figure 3. Nitrogen sorption isotherm of cement paste cured under different relative humidity for 9 months (left) and BET surface area of cement paste (right).

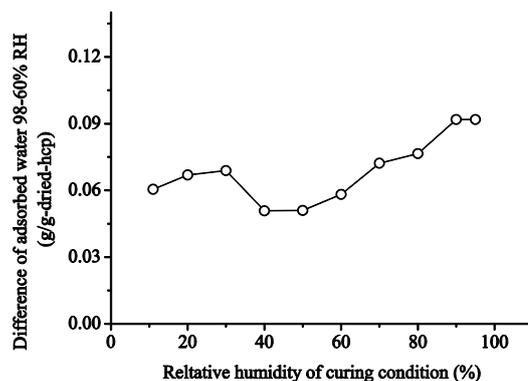
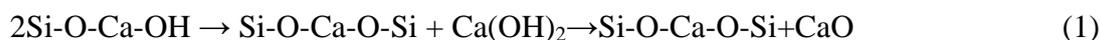


Figure 4. dW_{98-60} versus relative humidity of curing condition.

It should be noted that the LGP is increased in the range below 40%RH of curing condition as it is seen in Figure 4, while no such trend is confirmed in Figure 3 right. Therefore, the regenerated LGP is only accessible by water vapor and not accessible by nitrogen. Regeneration of LGP can be attributed to the decrease of S_{H_2O} , because the decrease of S_{H_2O} indicates consolidated globules which can not allow the penetration of water vapor. This

consolidate globule indicates an increase of a density of globule and a shrinkage of globule at the same time. Thinning process of globule may produce another LGP between them.

The mechanism of decreasing trend of S_{H_2O} as the decrease of relative humidity of curing condition is a question. Silicate structure of hydrated alite paste under different relative humidity curing condition was examined using quantitative gel permeation chromatography of the trimethylsilyl silicate derivatives by Parrot and Young (1981). According to their results, silicate chain will not be extended by drying. This fact implies that silicate chain can not be considered as the factor of S_{H_2O} change. Therefore, the remained problem is Ca behavior. Regarding Ca in C-S-H, presence of Ca-OH in C-S-H has been reported by Thomas et al (2003) based on an experimental result by inelastic neutron scattering technique. They concluded that C-S-H is the mix of Jennite type structure and tobermorite structure, and Ca-OH is from the Jennite type structure. On the other hand, Brunet et al. used ^{29}Si heteronuclear chemical shift correlation NMR technique and it was reported that Ca-OH is located near Q^1 , Q^2 , and Q^{2p} Si site and this indicates that Ca-OH is not only in Ca-layer but also in interlayer, and the hypothesis of existence of Si-O-Ca-OH is proposed (2004). In the high density C-S-H, which is mainly Ca-leaching results of alite or belite, may have much Ca-O-Si-OH can be remained in it. Indirect evidence of different stability of Ca condition can be observed in dynamic-TG analysis. Figure 5 shows the experimental results of dynamic-TG of cement paste cured 11%RH, 40%RH, and 95%RH respectively. As it is shown in this figure, cement paste cured at 95%RH shows blur drop curve around 375 °C, while straight and sharp drop is seen in the case of cement paste cured at 11%RH. This trend implies that there are different types of Ca-OH. The possible reaction is:



This equation surmises that the C-S-H which has a Ca/Si ratio and may be a result of Ca leachin results from alite or belite have Si-O-Ca-OH bonds and drying process proceeds the precipitation of CH from such bonds and making the Ca-layer in C-S-H at the same time.

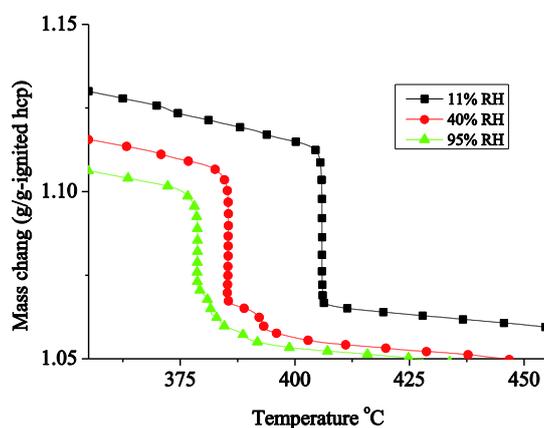


Figure 5. Dynamic TG curve of cement paste cured under 11%RH, 40%RH and 95%RH for 1 year. 105°C holding for 7 hours is executed before this analysis to avoid different water release rate from C-S-H.

Therefore, thinning distance of two C-S-H is yielded due to drying by precipitating CH and making Ca-layer. This reaction also reduces the sites of water adsorptions and produces LGP

between the globules. Based on the hypothesis, the change of nano-scale structure is summarized in Figure 6, and expected changing of each pore volume in cement paste and C-S-H property change are shown in Figure 7.

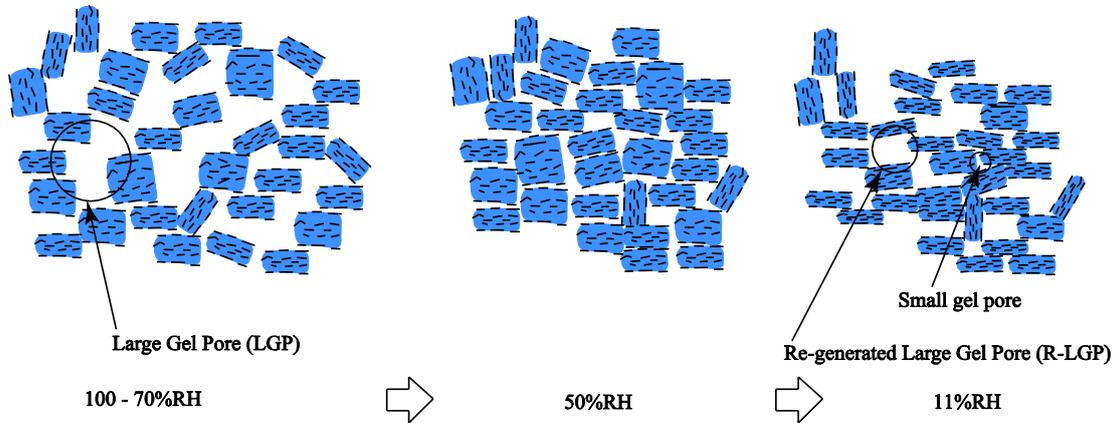


Figure 6. Schematic of nano-scale change of microstructure in cement paste.

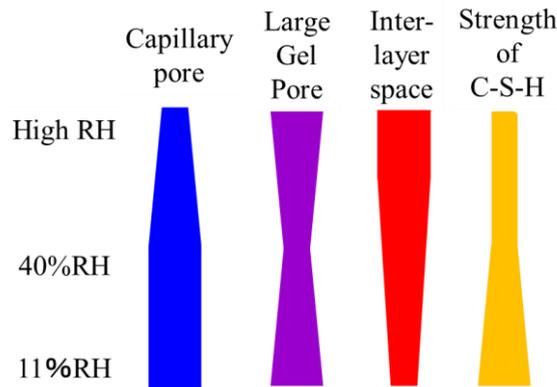


Figure 7. Schematic of volume change of different types of pores in cement paste due to drying and strength change of C-S-H. Width of band shows relative values of volume of pores or strength.

Under the first desorption process, globule clusters which are generally located around the unreacted cement core is packed due to capillary pressure or solution and re-precipitation process of C-S-H. LGP is collapsed during this process and, therefore, S_{N_2} shows decreasing trend and dW_{98-60} shows decreasing trend as well. At the same time, capillary pore which is the large pore located between hydrated cement agglomerates is enlarged. These phenomena take place from saturated condition to 40%RH condition. In the desorption process less than 40%RH, thinning of globule takes place with precipitating CH and making Ca-layer. In addition, this thinning process causes the re-generation of LGP, and probably, the strength of C-S-H is increased. At the same time, S_{H_2O} is dramatically decreased and S_{N_2} can not be changed because nitrogen can not penetrate the inside of globule clusters, while water vapor can go inside and then, dW_{98-60} shows increase trend.

Figure 8 shows the relationship between bending strength of cement paste and relative humidity of curing condition. There are two trends. One is the decreasing trend, which is observed from 90%RH to 40%RH. This is explained by the increasing of capillary pore and

stress concentration around enlarged capillary pore caused the decrease in nominal bending strength of cement paste. The other one is increasing trend, which is observed from 40%RH to 11%RH. This attributes to the strength increase of C-S-H caused by making Ca-layer. Decreasing trend by enlargement of capillary pore and increasing trend by thinning of globule and increasing of strength of C-S-H are overlapped and, then, the complex behavior of bending strength change under different relative humidity of curing condition is produced.

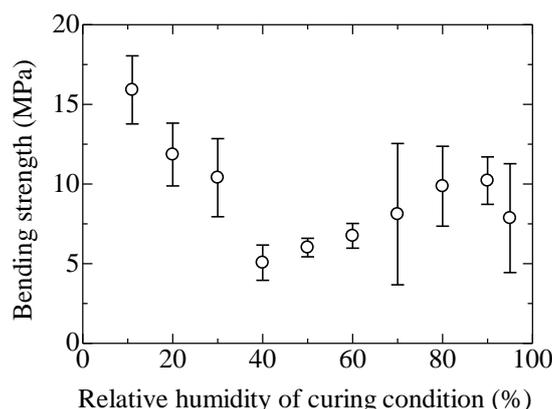


Figure 8. Bending strength of cement paste cured under different relative humidity for 1 year.

COCLUSIONS

Water vapor sorption isotherms, nitrogen sorption isotherms, thermogravimetry, and bending strength of matured cement pastes cured under different relative humidity are measured. Under the first desorption process, BET surface area by nitrogen sorption and incremental water sorption amount from 60%RH to 98%RH shows decreasing trend. These experimental results indicated that globule clusters which are generally located around the unreacted cement core is packed due to capillary pressure or solution and re-precipitation process of C-S-H. Large gel pore which lies among globules is collapsed during this process. At the same time, capillary pore which is the large pore located between hydrated cement agglomerates is enlarged. This enlargement of capillary pore causes the decrease in nominal bending strength of cement paste. These phenomena take place from saturated condition to 40%RH condition. In the desorption process less than 40%RH, dramatic decrease in BET surface area by water vapor sorption and increasing trend of incremental water sorption amount from 60%RH to 98%RH were observed. These experimental results imply that thinning of globule takes place. In addition, this thinning process causes the re-generation of large gel pore, and the strength of C-S-H is increased. The increase of nominal bending strength of cement paste was experimentally confirmed, therefore, the effect of increase in strength of C-S-H overcomes the effect of enlargement of capillary pore. The mechanism and atomic reaction causes thinning of globule remains as a question. The possible hypothesis of this reaction is that C-S-H with high Ca/Si ratio has Si-O-Ca-OH group and these group react as $2 \text{ Si-O-Ca-OH} \rightarrow \text{Si-O-Ca-O-Si} + \text{Ca(OH)}_2$.

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