

## **Bending strength and Young's modulus changes of hardened cement paste using high early strength Portland cement after long-term drying**

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### **ABSTRACT**

In the long-term operation of nuclear power plant (NPP), integrity evaluation of concrete structures to be extended into the future is needed. In order to accurately assess, it is important to understand physical property changes of concrete under long-term drying. We investigated changes in the physical property of hardened cement paste (hcp) under different drying and heating conditions.

In this experiment, we used high-early-strength Portland cement as a representative of alite-rich ordinary Portland cement, in hcp specimens. Samples dried in the range from 11% to 95% RH at 20 °C, and heated less than or equal to 90 °C. The changes in flexural strength and Young's modulus, water vapor sorption properties were evaluated by bending test and water vapor sorption measurement.

During the first drying process, calcium silicate hydrate (C-S-H) which is major hydration product occurs colloidal alteration. From the experimental results after 1 year drying, flexural strength and Young's modulus decreased for saturated state at 20 °C to medium humidity, increased for medium humidity to 11% RH. At heating condition up to 90 °C, Young's modulus was almost equal to 11% RH, and bending strength showed a variation in a range.

These changes in the physical properties were explained by the relationship of specific surface area and water sorption apportionments obtained from water vapor sorption test.

### **INTRODUCTION**

In the long-term operation of nuclear power plant (NPP), integrity evaluation of concrete structures to be extended into future is needed. In order to accurately assess, it is important to understand physical property changes of concrete under long-term drying or heating. In NPPs, the temperature of the concrete is regulated for normal long-term operation. The concrete surface temperatures should not exceed 65 °C except for localized areas, such as around penetrations, which are allowed to reach temperatures of up to 90 °C (American Concrete Institute,(2001), ACI-ASME Joint committee). The regulations are based on experimental data that shows a drop in saturated in lime water or sealed conditions. These data show that concrete components affect the changes in the behaviour of the compressive strength of concrete in response to drying or heating.

The mechanism behind these effects is important for cement chemistry and concrete science. Concrete is composed of an aggregate and cement paste. Maruyama et al. (2014) examined the concrete components, such as cement paste and coarse aggregates, and the compressive strength and Young's modulus of mortar and concretes containing different sizes or types of aggregates. They summarized that the change in compressive strength of concretes under various drying or heating conditions was explained by the behaviour of the cement paste matrix and damage accumulation caused by differences in volume changes between the aggregate and mortar. In addition, the mortar shrinkage is the main factor in the accumulation of damage during drying, and the shrinkage of cement paste, which is the driving force of mortar, is one of the key factor of change in the strength of concrete. And changes in the strength of cement paste affect the strength of concrete, because the hardened cement paste located in the load

bearing path directly contribute to the concrete strength. So the concrete strength under drying or heating conditions is governed by the properties of the hardened cement paste.

From the above, pertaining to the effects of heating and drying conditions, from sealed conditions to heating at 90 °C, data on the strength and Young's modulus of cement paste should directly contribute to the management of aging NPPs, and the type of cement paste affects the change in the concrete properties under drying or heating conditions, through the drying shrinkage and the strength of the cement paste. In this study, we investigated the bending strength and Young's modulus changes of cement paste, which is used high-early-strength Portland cement as a representative of alite-rich ordinary Portland cement. In addition, water vapor sorption measurements were performed to evaluate microstructural changes of cement paste during drying and heating.

## EXPERIMENTAL PROCEDURE

### *Material and sample preparation*

In this study, high-early-strength Portland cement was used. The chemical composition, physical properties and mineral composition of unreacted cement are shown in Table 1 and Table 2. The mineral composition was determined by powder X-ray diffraction measurement and the Rietveld analysis.

The mixture proportion of cement paste was designed the water-cement ratio to 0.55. The paste was mixed in a 20L Hobart mixer for 3 min after the water was added, and then for a further 3 min after the paste was scraped from inside the mixer. All the materials were stored in a thermostatic chamber at  $20 \pm 1$  °C for 1 day prior to mixing. The mixing was performed at room temperature (ca. 20 °C) and the specimens were then immediately moved to a thermostatic chamber again. To minimize segregation, the paste was remixed every 30 min until 6 h. After remixing, the specimens were cast into a set of  $3 \times 13 \times 300$  mm<sup>3</sup> slab molds which were covered by polyvinylidene-chloride wrap and wet papers to avoid water loss from the specimens. The molds were placed in a thermostatic chamber at  $20 \pm 1$  °C.

They were demolded after 3 days, immersed in lime-saturated water for 1 year, and then dried under the humidity controlled chamber for 1 year. The RH in the chamber was controlled with a sodium hydroxide solution (Maruyama et al. (2010), Jennings(2004), Stokes and Robinson (1949)). And sodium hydroxide was used to avoid carbonation. The target RHs were 95%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 11% at  $20 \pm 1$  °C. For the specimens heated at 40 to 90 °C, they were dried at 11% RH ( $20 \pm 1$  °C) for 6 months from the start of drying, and after achieving equilibrium state, they were heated in each heating chamber for next 6 months. The heating temperatures were 40, 50, 60, 70, 80, and 90 °C. During the heating at each thermal chamber, the specimen was placed in aluminum bag and the internal air was exchanged through the carbon dioxide adsorbent.

Thereafter, the specimen is expressed as H55 as a whole, and is distinguished by dry humidity or heating temperature.

Table 1: Chemical composition and physical properties of high early strength Portland cement

Density (g/cm <sup>3</sup> )	Blain (cm <sup>2</sup> /g)	ig.loss (%)	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 <sup>-</sup> (%)
3.14	4400	0.78	20.46	4.96	2.49	65.71	1.48	2.9	0.2	0.33	0.014

Table 2: Mineral composition of high early strength Portland cement

C <sub>3</sub> S (%)	C <sub>2</sub> S (%)	C <sub>3</sub> A (%)	C <sub>4</sub> AF (%)	Periclase (%)	Bassanite (%)	Gypsum (%)
66.0±0.6	14.3±0.8	6.7±0.2	8.8±0.1	0.7±0.1	2.96±0.2	0.56±0.1

## ***Experimental methods***

### ***Bending test***

The bending strength and Young's modulus of the  $3 \times 13 \times 300 \text{ mm}^3$  thin slab specimens was obtained with a three-point bending test. The span was 60 mm and the center of the span was loaded. An average value was obtained from more than five experiments. The bending strength was evaluated by the following Equation 1,

$$f_b = P \cdot \frac{l}{4} / \frac{I}{h/2} \quad (1)$$

Where  $f_b$  is the bending strength ( $\text{N/mm}^2$ ),  $P$  is the maximum load (N),  $I$  is the moment of inertia ( $\text{mm}^4$ ), and  $h$  is specimen thickness (mm).

### ***Water vapor sorption test***

Water vapor sorption measurements were conducted by the volume method using a water vapor sorption analyzer (Hydrosorb 1000, Quantachrome). A sample (~20 mg) was used for each measurement at 20 °C, with a pressure tolerance of 0.05 mmHg and a time tolerance of 120 sec. The measurement points on the adsorption and desorption branches were at  $p/p_0 = 0.05$  intervals up to 0.95, and ended at 0.98 (RH = 98%). The specific surface area ( $S_{H_2O}$ ) of adsorption branch was calculated using BET theory (Brunauer and Emmett, Teller (1938)) with a water molecule section value of  $0.114 \text{ nm}^2$  (Mikhail and Selim (1966)). The samples were crushed and powder with diameter of 25 – 75 $\mu\text{m}$  was used for this analysis. For pre-treatment, the samples were dried using a vacuum pump (theoretical minimum pressure of  $6.7 \times 10^{-2} \text{ Pa}$ ) and heated to 105 °C with a heating mantle for 30 min.

### ***Water content measurement***

The saturated water contents of the specimen after drying and heating were measured. The specimen (ca. 0.5 g) was re-saturated under a vacuum pump for 1 hour, and then placed in a container connected to a carbon dioxide adsorbent, and dried in a 105 °C oven for 7 days.

## **RESULTS AND DISCUSSIONS**

### ***Bending strength and Young's modulus***

Figure.1 shows the bending strength of the cement paste as a function of RH and temperature. In the range of drying at 20 °C, from saturated condition to 95% RH, the bending strength increased slightly, and then decreased until 40% RH. After that, the strength increased significantly from 40% to 11% RH. Maruyama et al. (2014) reported the bending strength of white Portland cement paste (W/C = 0.55) dried at various relative humidity at 20 °C for 1 year. Compared to data of white Portland cement paste, even in this experiment with high-early-strength Portland cement and W/C = 0.55, the results that the bending strength decreased from high humidity to 40% RH and then increased again at lower humidity than 40% RH was consistent.

In the heating conditions, the bending strength decreased at 40 °C, then increased until 60 °C. Above 60 °C, the strength decreased again but almost the same value was obtained at 70 ~ 90 °C. The bending strength change during heating showed variations, but it was found that the strength is the minimum value at 40% RH and increased under more severe drying conditions. In this study, the bending strength at heating conditions is similar as that of 11% ~ 30% RH at 20 °C.

Figure.2 shows the Young's modulus of the cement paste. In drying at RHs, changes in the Young's modulus are similar to the changes in the bending strength. In the heating conditions, the Young's modulus has almost no change except in 40 °C, and are almost the same value as that of 11% RH at 20 °C.

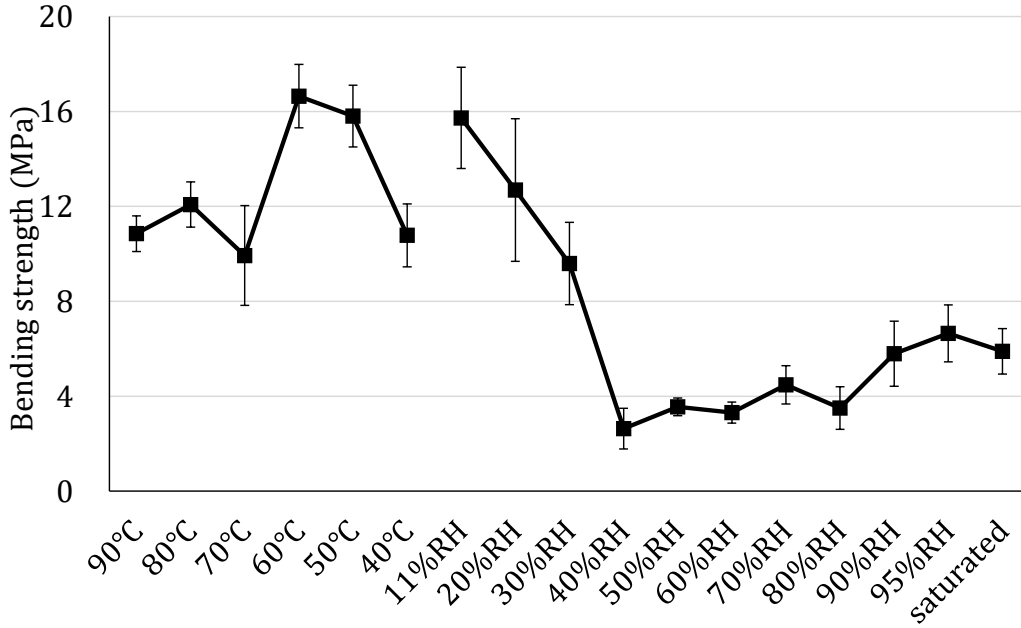


Figure.1. Bending strength of cement paste under different heating or drying conditions.

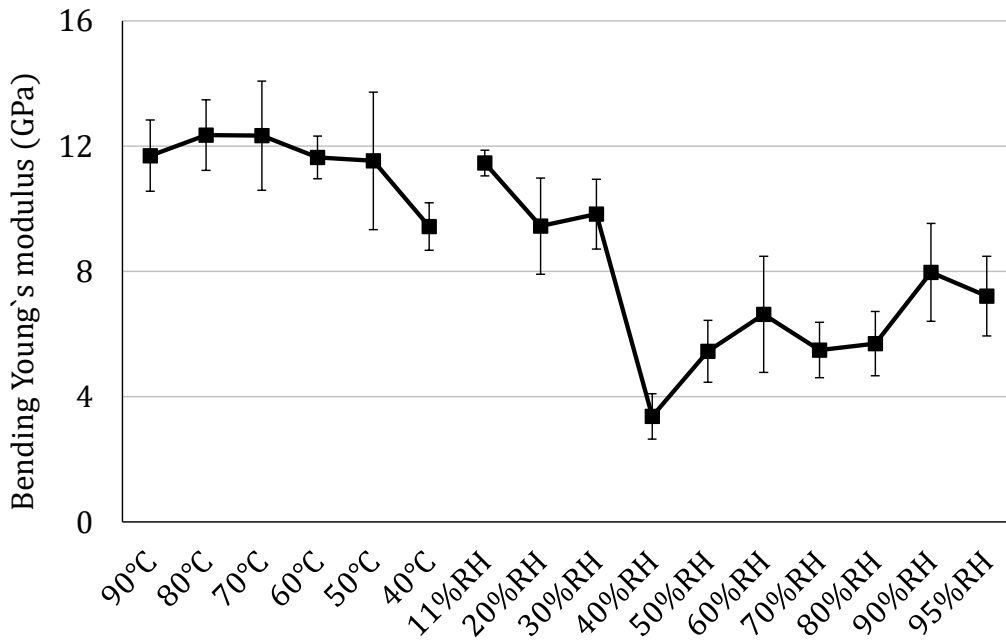


Figure.2. Young's modulus of cement paste under different heating or drying conditions.

### ***Water vapor sorption***

The experimental water vapor adsorption isotherms of the cement paste after drying or heating are shown in Figure.3. In Figure.3 (a), there are listed samples dried at various RHs. The sorption isotherms of samples from H55-95%RH to H55-80%RH showed no significant difference from  $p/p_0 = 0$  to 40%. In this  $p/p_0$  range, sorption amount of samples decreased as the drying RH decreased. The sorption isotherms above  $p/p_0 = 0.4$  showed different trends depending on the drying RH. The sorption amount decreased as the drying RH decreased, especially from H55-80%RH to H55-60%RH, sorption amount changed greatly. In addition, the sorption amount of the sample drying lower RH than 40% increased at higher  $p/p_0$  ranges. The sorption isotherms of heated samples are shown in Figure.3 (b). In this figure, sorption amount of the samples clearly decreased as the temperature increased.

Figure.4 shows the  $S_{H_2O}$  data for the samples as a function of drying or heating conditions. The  $S_{H_2O}$  decreased from saturated condition to 90 °C. This trend was consistent with the data reported by Maruyama et al. (2014). They also pointed out that the reduction of  $S_{H_2O}$  from 95% to 40% RH was almost the same value as that of the surface area calculated from nitrogen sorption, so the reduction of  $S_{H_2O}$  of this humidity range may mainly correspond to the decrease of the nitrogen accessible mesopores. In addition, the decrease of  $S_{H_2O}$  at less than 40%RH and heating conditions indicates irreversible behaviour of the interlayer hydrate water of C-S-H. In Figure.4, the decrease of  $S_{H_2O}$  is very small from saturated state to 70% RH, and can be seen clearly at 70% RH below or heating conditions.

### ***Water sorption apportionments***

Based on the sorption isotherms and the re-saturated water content, water sorption apportionments were obtained. The water sorption apportionment was classified into three pore types by the pore diameter calculated from the Kelvin equation at 20 °C. One is macropore, which can be evaluated by the incremental water sorption from  $p/p_0 = 0.95$  to re-saturated conditions ( $dW_{95-sat}$ ), another is mesopore, which is the incremental sorption from  $p/p_0 = 0.40$  to 0.95 ( $dW_{40-95}$ ). The other is micropore which is incremental sorption from dry conditions at 105 °C to  $p/p_0 = 0.40$  ( $dW_{0-40}$ ). Note that pore diameter when  $p/p_0 = 0.40$  is about 2.5 nm, and when  $p/p_0 = 0.95$  is about 50 nm. So  $dW_{95-sat}$  corresponds to capillary pore,  $dW_{40-95}$  includes the size of large and small gel pores among the C-S-H globules in CM-II (Jennings (2008)), and  $dW_{0-40}$  corresponds to interlayer spaces of C-S-H and small gel pores.

Figure.5 shows the water sorption apportionments as a function of drying RHs or temperature. The amount of micropores ( $dW_{0-40}$ ) increases from saturated state to around 80% RH, then decreases continuously until 90 °C. Mesopores ( $dW_{40-95}$ ) decreases until around 50% RH, then increases as drying RH decreases. In the heating, the amount of mesopores slightly decreases as temperature increases. In case of macropores ( $dW_{40-95}$ ), it decreases from saturated state to 95% RH, then increases until 60% RH. Below 60% RH, it has roughly no change. At heating conditions, the amount of macropores is roughly the same from 40 °C to 80 °C, then increases at 90 °C. These microstructural changes were produced by the colloidal behaviour of C-S-H. The aggregation of C-S-H globules or particles is more compacted and the interlayer space of C-S-H is thinned under drying or heating process. During drying and heating, some interlayer spaces are destroyed by the compaction of C-S-H aggregation and this is the reason of the reduction of  $S_{H_2O}$  during drying or heating as shown in Figure.4. The increased mesopores in Figure.5 are due to this compaction.

Maruyama et al. (2014) summarized that the changes in strength and Young's modulus of white Portland cement paste are explained by a combination of the colloidal and porous properties of the cement paste, in which the decrease in strength from high RH to 40% RH was due to the increase in the number of macropores because of the consolidation of globule clusters, and the increase in strength below 40% RH was due to densification of the C-S-H globules and the resulting increase in the strength of the solid phase. In our present study, results of high-early Portland cement paste can be also explained by the same mechanism.

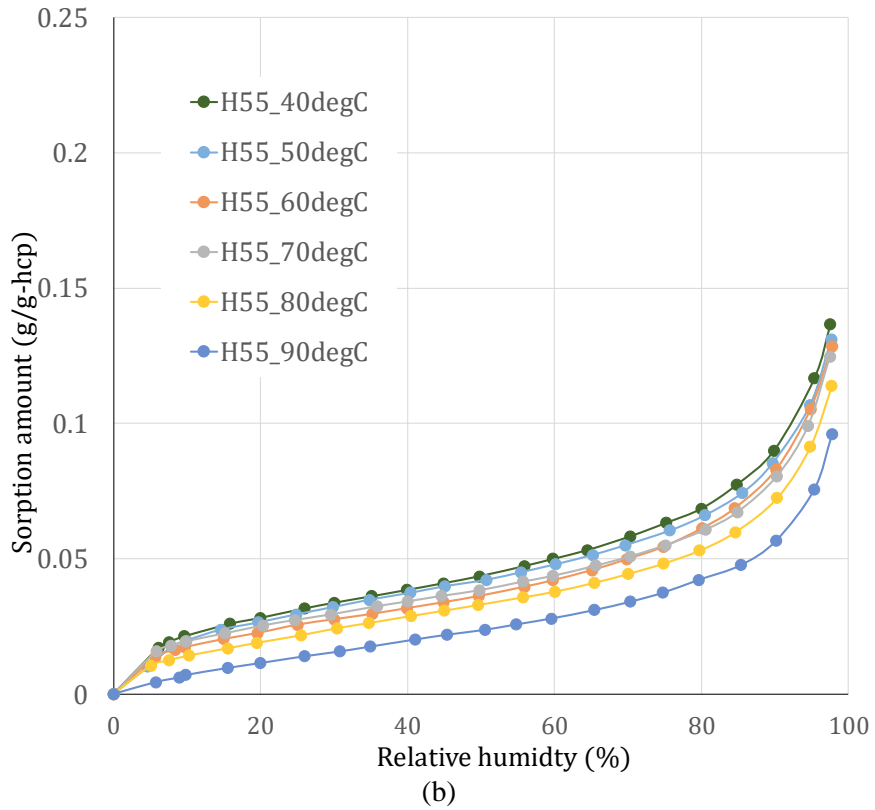
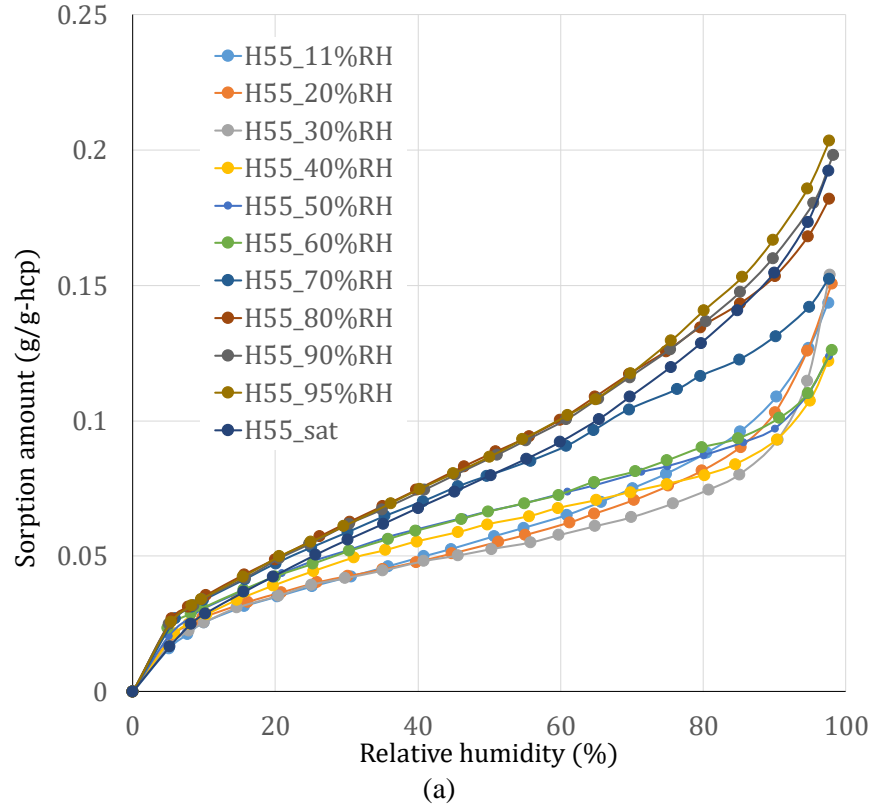


Figure.3. Water vapor adsorption isotherms (a) samples after drying at 20 °C, (b) samples after heating

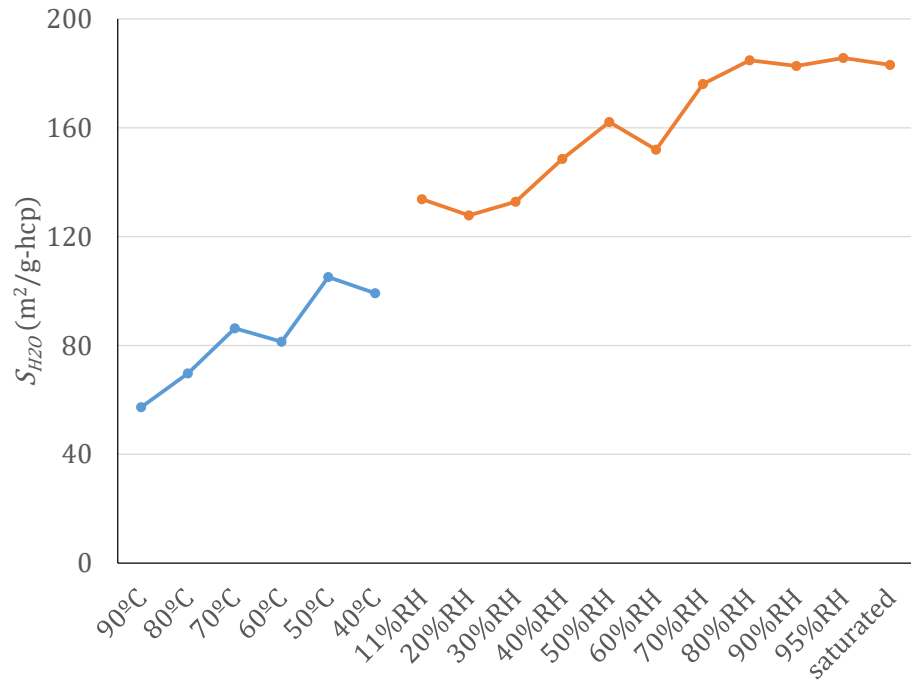


Figure.4. Specific surface area calculated from water vapor adsorption branches.

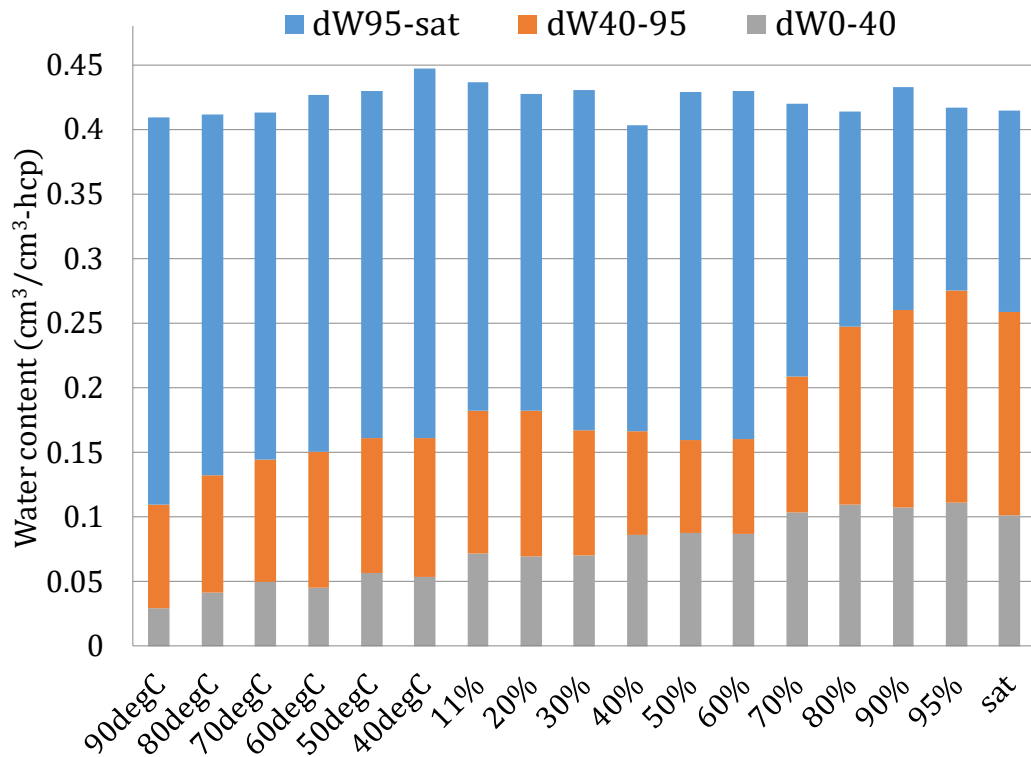


Figure.5. Water sorption apportionments of samples.

## CONCLUSION

In this study, the changes in the physical property of cement paste under different drying and heating conditions were investigated. Bending test and water vapor sorption measurements on high-early-strength Portland cement paste with W/C = 0.55 were performed after 1 year drying or heating, the following new findings were obtained:

- 1) After drying at several RHs at 20 °C, from saturated condition to 95% RH, the bending strength increased slightly, and then decreased until 40% RH. After that, the strength increased significantly from 40% to 11% RH. In the heating conditions, the bending strength decreased at 40 °C compared with strength at 11%RH (20 °C), then increased until 60 °C. Above 60 °C, the strength decreased again but almost the same value was obtained at 70 ~ 90 °C.
- 2) The Young's modulus changes in drying conditions are similar to the changes in the bending strength. In the heating conditions, the Young's modulus has almost no change except in 40 °C, and are almost the same value as that of 11% RH, 20 °C.
- 3) The specific surface area calculated from water vapor sorption decreases slightly from saturated state to 70% RH, and decreases clearly at 70% RH below or heating conditions. This decrease is result from compaction of C-S-H.
- 4) From the water sorption apportionments based on water vapor sorption and re-saturated water content, mesopores (pore diameter:2.5~50nm, correspond to large and small gel pores among the C-S-H globules) decreases until around 50% RH, then increases as drying RH decreases. In the heating conditions, the amount of mesopores slightly decreases as temperature increases. The increase of mesopores at 50% RH below results from compaction of C-S-H. Macropores (correspond to capillary pores) decreases from saturated state to 95% RH, then increases until 60% RH. Below 60% RH, it has roughly no change. At heating conditions, the amount of macropores is roughly the same from 40 °C to 80 °C, then increases at 90 °C.
- 5) The changes in strength and Young's modulus of cement paste can be explained by a combination of the colloidal and porous properties of the cement paste. The decrease in strength from high RH to 40% RH was due to the increase in the number of macropores because of the consolidation of globule clusters, and the increase in strength below 40% RH was due to densification of the C-S-H globules and the resulting increase in the strength of the solid phase. And this mechanism is consistent in different cement type, in case white Portland cement and high-early-strength Portland cement.

## ACKNOWLEDGEMENTS

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