

# Effects of Humidity Condition for Drying of the Sample Preparation on the Pore Structure of the Hardened Portland Cement Paste

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## 1. Introduction

Pore structure of concrete is a most important character in order to discuss the durability of concrete. Pore size distribution of hardened cement paste or concrete is generally measured by means of mercury intrusion method. Cement paste or concrete is usually cured in water. Free water is existed in pore in the hardened body. Free water in the pore must be removed by appropriate drying method before measuring. The many studies are reported for drying method of sample preparation [1],[2],[3]. Method of D-dry or method of drying at 105C are often used for sample preparation. Hydrates such as Aft, AFm and C-S-H are partly dehydrated by heating at 105C or exposing in a low humidity conditions [4],[5]. Hydrates and pore structure are changed by the strong drying method of preparation such as D-dry or dried at 105C. In contrary, pore structure cannot measure by weak drying condition because free water in the pore is not removed. Measurement system without changing the pore structure during the sample preparation is necessary for measuring the pore structure of cement paste and concrete. Drying by humidity controll is supposed to be good method for preparation of sample, because concrete is usually exposed in various humidity conditions. But there is little study by humidity controll for drying method of sample preparation for mercury intrusion method

Authors discussed the pore size distribution of hydrated cement paste exposed in the various humidity condition [6],[7]. In this study, the effect of humidity condition for drying the sample on the pore structure of the hardened cement paste is discussed, and optimum drying condition of sample preparation for mercury intrusion method is suggested, then the effects of additives on the pore structure is discussed by the paste with various additives cured for 10 years.

## 2. Experimental procedure of cement paste without additives

### 2.1 Sample

Ordinary Portland cement used in the experiments was prepared to cement association of Japan, which did not include any pozzolanic or filler particles. Blaine specific surface area of the cement was  $327\text{m}^2\text{kg}^{-1}$ . Chemical composition of the cement is listed in Table 1. Cement and water were mixed by water and cement ratio of 0.25, 0.3, 0.35 and 0.4. respectively, and then the pastes were cured in water at  $20\text{C}$  for 6 years.

Table 1 Chemical composition of the Portland cement

Sample	Ig.loss	Insol	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	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cl
Cement	0.6	0.1	21.3	5.3	2.6	64.4	2.2	1.9	0.28	0.6	0.37	0.2	0.1	0.007

## 2.2 Method of sample preparation and measurement of pore structure.

The hardened cement pastes cured for 6 years were cut to small plate of  $20\times 20\times 10\text{mm}$ . The hardened pastes were dried as following 2 series

- (1) Each hardened paste was dried at 40, 50 and 105 for 24 hours without humidity controll, respectively.
- (2) Each hardened paste was exposed in the different humidity conditions such as RH81, RH66, RH44 and RH15% at  $20\text{C}$  for 8 months, respectively.

The Humidity was controlled by the saturated aqueous solution of salt in the each desiccator. The used salts were as follows. RH81%: ammonium sulfate. RH66%: sodium nitrite. RH44%: potassium carbonate. RH15%: lithium chloride. The samples were periodically took off from the each desiccator. Weight of them was measured and backed in the desiccator.

Figure 1 shows changes in weight loss of the samples of  $W/C=0.4$  exposed in various humidity condition with time. The weight loss was large at the early exposing time and proceeded gradually. It took long time until the weight had not decreased. When the each sample was exposed for 8 months, the weight seemed to become nearly constant value.

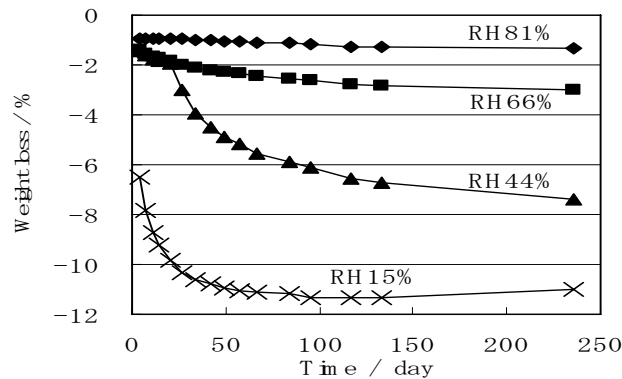


Fig.1. Changes in weight loss of the samples of  $W/C=0.4$  with time exposed in various humidity at at  $20\text{C}$

Table 2 shows the weight loss of the samples exposed in various humidity for 8 months. The larger weight loss occurred in the sample exposed in the lower humidity condition. The weight loss was less than 1% in the sample of W/C=0.25 exposed in RH81%. It was suggested that the large amount of free water existed in the pore. The large weight loss about 11% was observed in the sample of W/C=0.4 exposed in RH15%. In the sample, ettringite crystal changed to amorphous phase.

Measurement by means of mercury intrusion method was carried out as follows. After prepared with (1) and (2) series, each sample was crushed to size of 3.35-5.6mm, and the sample was evacuated for 5 minutes in the apparatus before mercury was added. This evacuation condition was sufficient time to remove air from the sample and to avoid the weight loss. The measuring pore size was between 10nm–100µm in diameter.

Table 2 Weight loss of the samples exposed in various humidity at 20°C for 8 months

	W/C			
	0.25	0.3	0.35	0.4
RH81%	0.77%	0.68%	0.56%	1.31%
RH66%	0.99%	1.77%	1.60%	2.99%
RH44%	2.63%	3.36%	4.54%	7.37%
RH15%	5.72%	6.98%	8.67%	10.98%

### 2.3 Results

Figure 2 shows the curves of cumulative volume of pore in the sample of W/C=0.4 treated with various drying conditions. The shape of curve and the amount of cumulative volume of pore varied widely with the drying conditions. In the case of the samples treated with week drying condition such as RH81% or RH66, the small amount of cumulative volume of pore was observed. The pore larger than 100nm was not observed and also the volume of pore smaller than 100nm was a little, the cumulative volume of pore larger than 10nm was 22 or 41 mm<sup>3</sup>cm<sup>-3</sup> respectively. In the case of the sample treated with RH44%, the large amounts of pore smaller than 100nm was observed, The volume of pore between 16 and 36nm was larger than that of the sample dried at 105°C. The cumulative volume of pore larger than 10nm was 117mm<sup>3</sup>cm<sup>-3</sup>. The shape of curve was convex in the range of small pore diameter, it suggested that the pore smaller than 10nm was little. In the case of the sample treated with RH15%, the pore smaller than 100nm was somewhat less than that of the sample treated by RH44%. The cumulative volume of pore larger than 10nm was 99mm<sup>3</sup>cm<sup>-3</sup>. The shape of curve was concave in the range of small pore diameter, it suggested that the large amount of pore smaller than 10nm existed. In the case of the sample dried at 105°C, the cumulative volume of pore larger

than 10nm was  $134\text{mm}^3\text{cm}^{-3}$  that was the largest value among the various drying conditions.

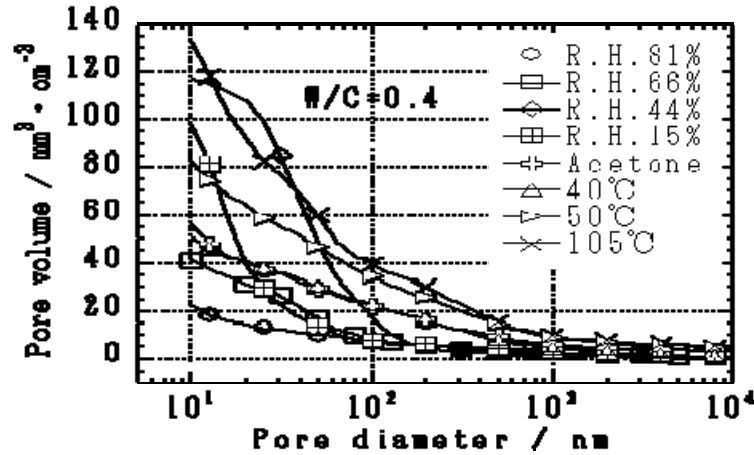


Fig.2. Curves of cumulative volume of pore in the sample of W/C=0.4 treated with various drying conditions

Figure 3 shows the pore size distribution of the sample of W/C =0.4 treated with various drying conditions. Both the distribution curve and the mode diameter of pore varied widely with the drying conditions. No peak was observed in the curve of the sample treated with RH81%. A small peak at 40nm was observed in the curve of the sample treated with RH66%, A large peak in the range of 20-40nm was observed in the curve of the sample treated with RH44%, The peak shifted to small pore diameter in comparison with the peak treated with RH15%. In the case of samples prepared by elevated temperature such as 40-100C, a small peak in the range of 100-1000nm was observed. This peak was not observed in the curves of the samples treated without heating. The pore in the range of 100 - 1000nm could be formed during the heat treatment. The curve of the sample dried at 105C was considerably

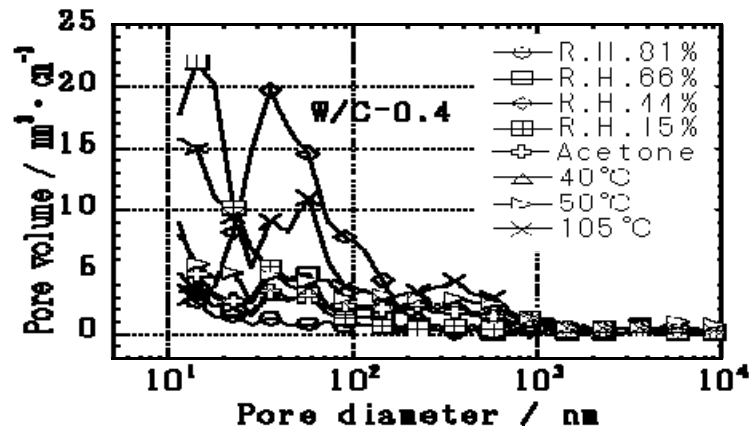


Fig.3. Pore size distribution of the samples of W/C=0.4 treated with various drying conditions

different from the other treatment. The pore structure was changed by decomposition of the hydrates and the shrinkage of the sample introduced by the strong drying process. Table 3 shows the amount of cumulative volume of pore larger than 10nm in the samples treated with various drying conditions. The larger amount of pore was observed in the sample of larger W/C ratio. The larger amount of pore was observed in the samples exposed in the lower humidity condition except RH44%. In spite of the weak drying condition in comparison with RH15%, the amount of pore volume in the sample treated with RH44% was the larger than that with RH15%.

Table 3 The amount of cumulative volume of pore larger than 10nm in diameter of the samples treated with various drying conditions

drying condition	water-cement ratio			
	0.25	0.3	0.35	0.4
RH81% 8months	6.8	6.5	4.9	21.9
RH66% 8months	5.3	5.7	42.0	40.9
RH44% 8months	8.8	31.8	59.5	117.3
RH15% 8months	10.3	29.3	52.5	99.2
Acetone	7.1	21.6	43.6	56.6
40C 24 hours	8.0	26.4	39.9	50.8
50C 24 hours	29.5	37.8	44.8	82.8
105C 24 hours	51.3	90.6	97.3	134.2

Unit : mm<sup>3</sup>/cm<sup>3</sup>

## 2.4 Discussions

### 2.4.1 Free water in the sample treated with various humidity

In order to discuss the free water in pore in the sample treated with various humidity, each sample treated with various humidity for 8months was dried at 105C for 24 hours, and then the weight was measured.

Figure 4 shows the weight loss of the humidity controlled samples dried at 105C for 24 hours. Weight loss was observed in the all samples, the drying at 105C for 24 hours was the stronger drying condition than that of the any humidity controll. In the case of the samples dried at 105C after treated with RH81%, the amount of weight loss varied with W/C of the samples. The amount of the weight loss was 20% in the sample of W/C=0.4 and 12% in the sample of W/C=0.25, respectively. In the case of the samples dried at 105C after treated with RH66%, the amount of weight loss also varied with W/C of the samples. The amount of the weight loss was 18% in

the sample of W/C=0.4 and 11% in the sample of W/C=0.25, respectively. In these weak drying condition, water remained in the pore and the weight loss was resulted by the evaporation water from pore during drying at 105C for 24 hours. In the case of the samples dried at 105C after treated with RH44%, the amount of weight loss was 10-12%, which varied a little with W/C of the samples. In the case of the samples dried at 105C after treated with RH15%, the amount of weight loss was 6-7%, which did not varied with W/C of the samples. The weight loss had to change with W/C, if there was free water remained in the pore. From the results, there might be no free water in the pore in the samples exposed in RH15%. In this study, ettringite crystal changed to amorphous phase exposed in RH15%. Dehydration or decomposition of C-S-H might be proceeded in the samples exposed in RH15%[4]. The amount of 6% of weight loss supposed to be resulted by the decomposition of hydrates or evaporation of water from the intercrystallite pore [8].

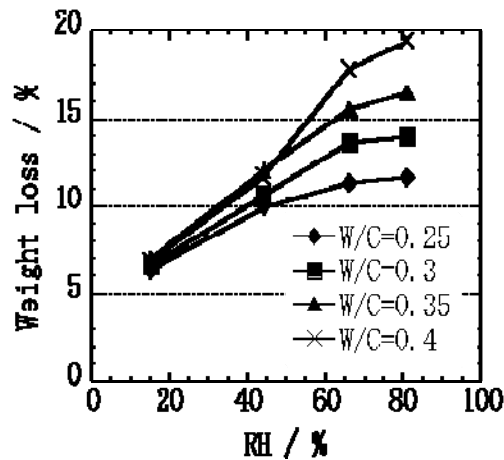


Fig.4. Weight loss of the humidity controlled samples dried at 105C for 24 hours

#### 2.4.2 Apparent porosity and the amount of pore smaller than 10nm

Pore volume and apparent porosity of porous materials are usually measured by means of Archimedes method. Total pore volume and apparent porosity can be measured by this method. In comparison between pore volume measured by Archimedes method and pore volume measured by mercury intrusion method, the amount of pore smaller than 10nm in diameter might be discussed. Measurement of Archimedes method was carried out as following process. At first, the weight of each sample treated with various humidity for 8months was measured ( $W_c$ ). And then the sample was put into water in a vacume desiccator. After evacuate air in the sample, the weight of sample in water was measured ( $W_i$ ). Then the sample was took off from the water, removed water on the surface of sample, the weight of sample was measured ( $W_s$ ). Apparent

porosity of the humidity controlled sample ( $P_c$ ) was calculated by following equation.

$$P_c = \left\{ \frac{W_s - W_c}{W_s - W_i} \right\} \times 100 \quad (\text{Eq. 1})$$

Figure 5 shows the apparent porosity of the humidity controlled sample measured by Archimedes method. The amount of  $P_c$  of the samples exposed in RH66% or RH81% was less than 2%. Most of the pore in the sample might be occupied with free water. In the case of the samples exposed in RH44%, amount of  $P_c$  was 1-12%, which varied with W/C of the samples. In the case of the samples exposed in RH15%, the amount of  $P_c$  was 4-16%, which varied with W/C of the samples.

Figure 6 shows the difference of the porosity of the humidity controlled samples between porosity measured by Archimedes method ( $P_c$ ) and porosity larger than 10nm measured by mercury penetrating method ( $P_{Hg}$ ). This value represents the volume of pore smaller than 10nm in which water was not filled by evaporation during the humidity control. The difference was small or almost zero in the samples treated with RH44, RH66 or RH81%. The pore smaller than 10nm was filled with water in the samples treated with RH44, RH66 or RH81%. However, the large amount of pore smaller than 10nm existed in the samples treated with RH15. These results agreed with the results of the pore size distributions.

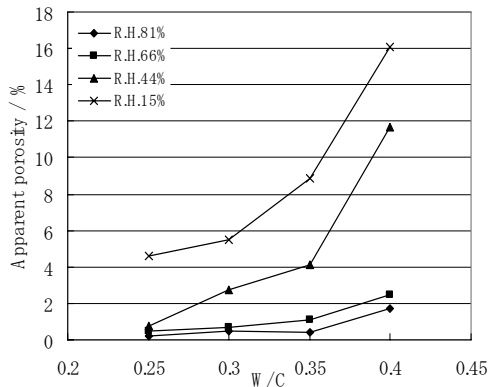


Fig.5. Apparent porosity ( $P_c$ ) of the samples measured by Archimedes method

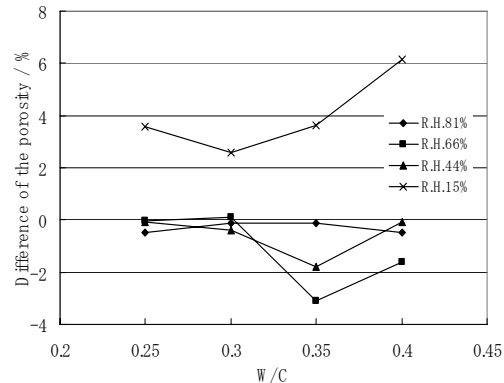


Fig.6. Difference of the porosity of the humidity controlled samples between ( $P_c$ ) and ( $P_{Hg}$ )

In order to discuss the relationship between weight loss and the volume of pore larger than 10nm in the sample treated with various humidity, the amounts of the weight loss from  $1\text{cm}^3$  of sample volume were calculated from the data listed in Table 2. The amounts of volume of pore larger than 10nm in  $1\text{cm}^3$  of samples were shown in Table 3.

Figure 7 shows the relationship between the weight loss and the volume of pore larger than 10nm in 1 cm<sup>3</sup> of the sample treated with various humidity. The amount of pore volume had to equal to the amount of the weight loss, unless both free water vaporized from the pore larger than 10nm and shrinkage occurred during the humidity controlling process.

The pore volume in the samples treated with RH81 or 66% was almost the same as the weight loss of the samples. It was suggested that the weight loss was resulted by evaporation of water from the pore larger than 10nm without shrinkage. In the case of the samples treated with RH15%, the amount of weight loss was much larger than the amount of volume of pore larger than 10nm. Shrinkage of the sample might be introduced by capillary force with the evaporation of water from the pore smaller than 10nm. The pore was shifted to small size, and then the pore larger than 10nm was decreased and the pore smaller than 10nm was increased. In the case of the samples of W/C=0.4 treated with RH15%, the pore volume was almost the same as the weight loss. It was suggested that the weight loss was resulted by evaporation of water from the pore larger than 10nm without shrinkage. In this case, the pore size distribution measured by the mercury intrusion method was supposed to be same as the pore size distribution of the sample in the water.

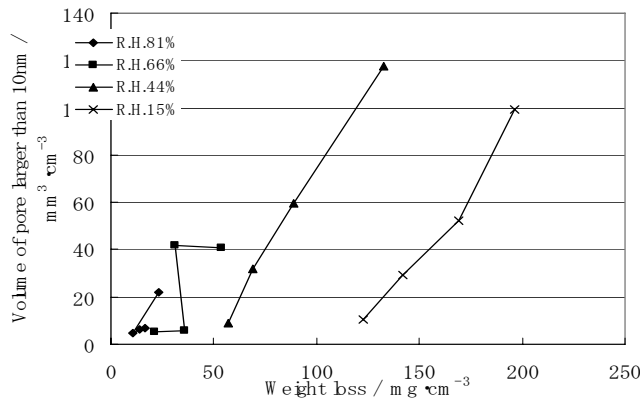


Fig.7. Relationship between weight loss and the volume of pore larger than 10nm in the 1 cm<sup>3</sup> of the samples treated with various humidity.

From the results and discussions above mentioned, It was found that the the drying condition of RH 66 or 81%H was too weak to dry for the sample preparation, because the large amount of free water remained in the pore in the samples. It was found that the drying condition of RH15% was too strong to dry for the sample preparation, because decomposition of hydrate occurred. It was suggested that the the drying condition of RH44% was the appropriate drying conndition, because litte free water remained in the pore in the samples and decomposition of hydrate did not occure.



### 3. Cement paste with additives cured for 10 years

#### 3.1 Sample and hardened paste preparation

Fine powders such as lime stone,  $\alpha$ -alumina, quartz, blast-furnace slag were used as additives. Specific gravity and specific surface area of the used powders are listed in Table 4.

Table 4 Specific gravity and specific surface area of the used powders

	Slag	Quartz	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	lime stone
density(g/cm <sup>3</sup> )	2.89	2.6	3.93	2.72
Specific surface area(m <sup>2</sup> /kg)	440	470	430	510

Cement and the fine powders were mixed with a mass ratio of 100:20 respectively. Pastes were prepared to W/C ratio of 0.4. W/S of the paste with additive was 0.33, which was smaller than that of the paste without additive. These pastes with or without additives cured in water at 20°C for 10 years.

#### 3.2 Characterization of the hardened pastes

Figure 8 shows the compressive strength of the hardened cement pastes. The each compressive strength of the hardened paste with additives was larger than that of the hardened cement paste without additives. The compressive strength of the hardened paste with slag or quartz was about 1.3 or 1.25 times of the hardened cement paste, respectively. The strength with lime stone or alumina was slightly larger than that without additives. Belite was observed little by XRD, almost of cement minerals reacted within the 10 year of curing. Peaks of Ca(OH)<sub>2</sub>, AFm and C-S-H were observed. And the height of peaks of additives such as quartz, calcite or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slightly decreased.

In order to discuss the reaction with additives, amount of Ca(OH)<sub>2</sub> was measured by means of differential scanning calorimetry (DSC). Figure 9 shows the amount of Ca(OH)<sub>2</sub> per cement content in the hardened pastes. The amount of Ca(OH)<sub>2</sub> in the all samples with additives was observed less than that without additives. In the case with slag or quartz, the amount of Ca(OH)<sub>2</sub> was decreased by the pozzolanic reaction between Ca(OH)<sub>2</sub> and slag or quartz. The amount of C-S-H was increased by the pozzolanic reaction. In the case with lime stone, Ca(OH)<sub>2</sub> decreased but C-S-H did not increase, because there was not silica component in the lime stone. Ca(OH)<sub>2</sub> reacted with lime stone and ettringite and produced AFm (3CaOA<sub>2</sub>O<sub>3</sub>CaCO<sub>3</sub>·11H<sub>2</sub>O) [7]. In the case with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, AFm phase was produced by reaction among Ca(OH)<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and water. C-S-H was not produced, because there was not silica component in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

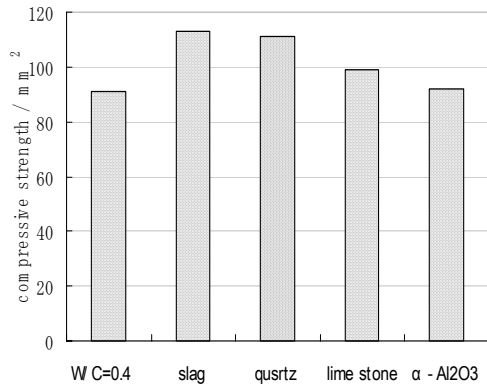


Fig.8. Compressive strength of the hardened cement pastes with or without additives cured at for 10years

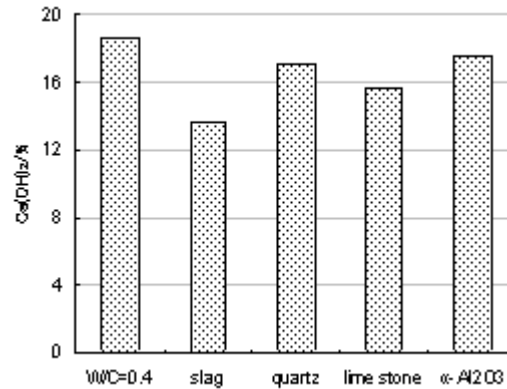


Fig.9. The amount of Ca(OH)<sub>2</sub> in the hardened cement pastes with or without additives cured at 20C for 10years

### 3.3 Method of sample preparation and measurement of pore structure

The hardened paste with additives exposed in RH44% at 20C for 225 days. The weight became nearly constant in the exposing time. Pore size distribution of these samples was measured by means of mercury intrusion method.

### 3.4 Results

Figure 10 shows curves of the cumulative volume of the pore in the sample of W/C=0.4 with various additives treated with RH44%. In the case of the sample without additives, the amount of pore larger than 100nm was the less than that of the sample cured for 6 years with RH44% treatment. Amount of the cumulative volume of pore larger than 10nm was about  $80\text{mm}^3\text{cm}^{-3}$ . The shape of curve was convex in the range of small pore diameter, which was similar to the curve of the sample of 6 years with RH44% treatment. In the case with lime stone or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, The convex curve was observed in the range of small pore diameter. The pore larger than 100nm was not observed. The shape of the curve and cumulative volume of pore did not change so much as that of the hardened cement paste without additives. The amount of cumulative volume of pore larger than 10nm was 87 and 91  $\text{mm}^3\text{cm}^{-3}$  respectively. In the case of the sample with quartz, amount of the cumulative volume of pore larger than 10nm was  $60\text{mm}^3\text{cm}^{-3}$ , which was the considerably less than that of the hardened cement paste without additives. In the case of the sample with slag, the pore larger than 10nm was observed little, amount of the cumulative volume of pore larger than 10nm was the less than  $20\text{mm}^3\text{cm}^{-3}$

Figure 11 shows the pore size distribution curves of the sample of W/C=0.4 with additives treated with RH44. Both curve and mode diameter of the pore varied widely with the additives. In the case of the samples without additives a small peak at 100nm and wide peak 20-40nm were observed. In the case of the samples with lime stone, a large peak at 60nm with shoulder at 40nm was observed. A large peak was observed at 20-40nm in the sample with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which was almost the same size without additives. A wide peak was observed at 15-30nm in the sample with quartz, which was shifted to small size compared without additives. No peak was observed in the curve of the sample with slag. The almost of pore might be smaller size than 10nm.

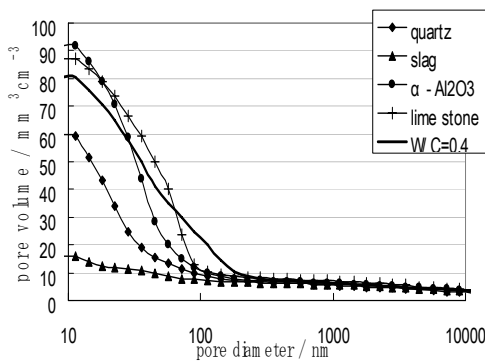


Fig.10. Cumulative pore volume of the sample of W/C=0.4 with various additives treated with RH44%

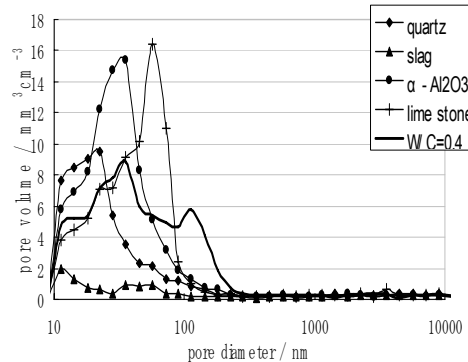


Fig.11. Pore size distribution curves of the sample of W/C=0.4 with various additives treated with RH44%

### 3.5 Discussions

In the case with slag or quartz, C-S-H was produced by the pozzolanic reaction, and the total pore volume decreased. And also, a pore was divided by C-S-H of which size was very small, and size of the pore became small. Amount of the cumulative volume of pore larger than 10nm decreased, and then the pore size distribution shifted to the smaller size. The compressive strength of the sample with slag or quartz was increased by both decrease of the total pore volume and the smaller size distribution of pore. In the case of with lime stone or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, C-S-H was not produced but AFm was produced by the reaction, and the total pore volume did not decrease. The large size of AFm crystal could not make the small size of pore, and the pore size distribution did not change so much as that of the hardened cement paste without additives. The compressive strength of the sample with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> might be slightly increased by the reaction.

#### 4. Conclusions

- (1) Pore size distribution changes considerably with exposed humidity condition.
- (2) The sample exposed in RH44% might be appropriate condition for preparation method for measuring pore size distribution by the means of mercury penetration method.
- (3) When C-S-H was produced by the pozzolanic reaction of additives such as slag or quartz, amount of the cumulative volume of pore larger than 10nm in the hardened pastes decreased, and the pore size distribution shifted to the smaller size.
- (4) When C-S-H was not produced by the reaction of additives such as lime stone or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, amount of the cumulative volume of pore larger than 10nm in the hardened pastes did not decrease, and the pore size distribution did not change so much as that of hardened cement paste without additives.

#### 5. References

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