

# The Measurement of the Pore Volume of Hardened Cement Mortar by the Water Vapor Desorption Method

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## ABSTRACT

This paper reports the suitability of the water vapor desorption method and the analysis of mortar samples for four types of cement. About six weeks was needed for measurement by the water vapor desorption method. During this time, only a small amount of hydration had occurred. The volume of pores between 6.3 and 12.4 nm diameter measured by the mercury intrusion porosimetry method was much smaller than that measured by the water vapor desorption method. The pore volumes between 1.0 and 12.4 nm in diameter were related to the amount of calcium hydroxide. With regard to the relationship between pore volumes and compressive strength in the 12.4 nm -10 μm pore diameter range, each type of cement had a different relative line.

## 1. INTRODUCTION

Although the mercury intrusion porosimetry method (MIP) is generally used to measure pore volumes of hardened cement, we measured them by the water vapor desorption method (WVD). Because of WVD can also measure smaller pore sizes than MIP.

There are two WVD methods, one is the chemical reagent method and the other is the controlled temperature method.

According to the theory of capillary condensation [1], the Kelvin radius is calculated with equation (1). The Kelvin radius is a function of relative humidity.

$$2r_k = \frac{-4sM}{dRT \ln(P/P_0)} \quad \text{— Equation (1)}$$

$r_k$  : kelvin radius(m)  
 $s$  : surface tension of water(0.07336 N/m)  
 $M$  : molecular weight of water(0.01802 kg/mol)  
 $d$  : density of water(1000 kg/m<sup>3</sup>)  
 $R$  : the gas constant(8.3144 J/mol.K)  
 $T$  : temperature(K)  
 $P/P_0$  : relative humidity  
( $P_0$ :saturated pressure of watervapor at temperature T)

## 2. WVD equipment

Figure 1 shows the equipment for the chemical reagent method.

Figure 2 shows the equipment for the controlled temperature method for creating different saturated water vapor pressures. The saturated water

vapor is made at a particular temperature and then introduced into a container at a higher temperature.

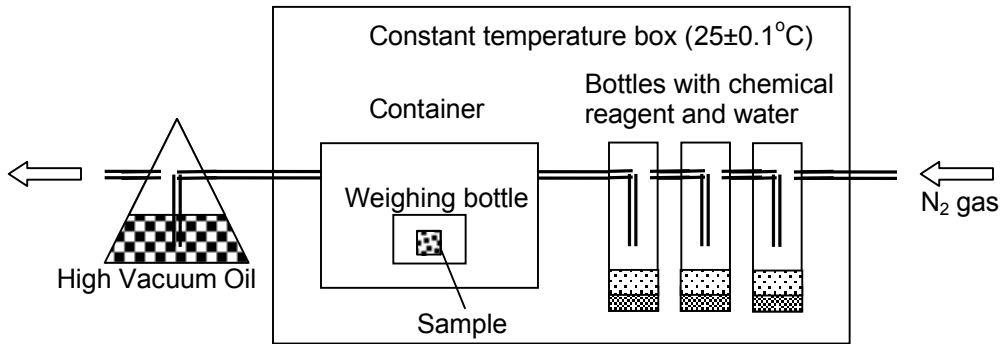


Figure 1. Equipment for the chemical reagent method

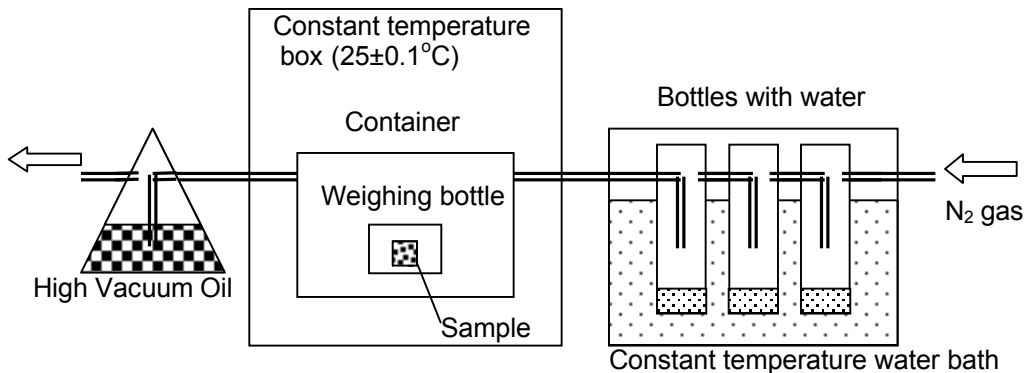


Figure 2. Equipment for the controlled temperature method

For example, in the controlled temperature method, when the temperature of the constant temperature water bath is 13.9°C, the saturated water vapor pressure ( $P_0 [13.9^\circ\text{C}]$ ) is 1588 Pa. When the temperature of the container is 25.0°C, the saturated water vapor pressure ( $P_0 [25.0^\circ\text{C}]$ ) is 3167 Pa. When the nitrogen gas that passed through the bottles with water at 13.9°C is introduced into the container at 25.0°C, the relative humidity in the later container can be calculated by equation (2).

$$\frac{P_0 [13.9^\circ\text{C}]}{P_0 [25.0^\circ\text{C}]} \times 100 = \frac{1588}{3167} \times 100 = \text{RH}50\% \quad \text{— Equation (2)}$$

In the controlled temperature method for creating different saturated water vapor pressures, the relative humidity can be changed at will.

### 3. EXPERIMENTAL

#### 3.1 CEMENT

Four kinds of cement were used. The symbols are as follows: H is high early strength Portland cement, O is ordinary Portland cement, M is moderate heat Portland cement and L is low heat Portland cement. The chemical composition and physical properties of the cements are shown in Tables 1, 2, 3, and 4.

Table 1. Chemical composition of cements in mass-%

	lg.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>
H	1.25	19.93	4.99	2.66	65.13	1.50	3.16
O	0.73	21.48	5.25	2.73	64.30	1.97	2.02
M	0.91	24.34	3.49	3.39	64.31	0.59	1.89
L	0.50	25.76	3.48	3.24	62.41	1.05	2.60

	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	SrO
H	0.23	0.40	0.26	0.33	0.04	0.05
O	0.27	0.49	0.25	0.23	0.09	0.11
M	0.24	0.51	0.17	0.06	0.04	0.03
L	0.30	0.32	0.20	0.12	0.14	0.03

\*Test method: JIS R 5204:2002

\*Ordinary Portland cement does not include additional inorganic materials

Table 2. Clinker phases calculated by Bogue's equation in mass-%

	Alite	Belite	Aluminate	Ferrite
H	67	6	9	8
O	54	21	9	8
M	43	37	4	10
L	23	57	4	10

\*CaO(correction) = CaO - SO<sub>3</sub> x0.7

Table 3. Density of cements and sand in g/cm<sup>3</sup>

H	O	M	L	Sand
3.13	3.16	3.19	3.24	2.64

\*Test method: JIS R 5201:1997

Table 4. Compressive strength of cement mortars in MPa(N/mm<sup>2</sup>)

	3days	7days	28days
H	48.2	57.3	65.4
O	26.4	45.6	63.6
M	21.1	33.0	58.2
L	7.7	11.9	52.5

\*Test method: JIS R 5201:1997 (ISO 679:1989)

### 3.2 Preparation of mortar samples

Mortar samples were prepared by the JIS R 5201:1997 (ISO 679:1989) method with a water to cement ratio (W/C) of 0.5 and a sand to cement ratio (S/C) of 3.0, and then cast in 4.0x4.0x16.0 cm molds.

Mortar samples were cured in water at 20°C. The curing times were 3, 7, and 28 days. After curing, the mortar samples were cut into 4.0x4.0x0.4 cm slices with a mortar cutter using water. Surplus water was removed from the sliced samples by placing them into acetone for several hours.

Each sliced sample was broken up into a number of small pieces with a plastic hammer. These small pieces were placed in a weighing bottle.

### 3.3 The relative humidity of the desorption experiments

The relative humidity given by Kelvin's equation for different pore sizes and methods are shown in Table 5. Pore sizes were selected for the following reasons:

- (1) Pores between 1.0 nm and 3.0 nm in diameter correspond to the gel pore size.
- (2) 6.3 nm diameter is the minimum size that can be measured by our MIP equipment.
- (3) 12.4 nm is about twice 6.3 nm.

Table 5. Pore size and relative humidity calculated by Kelvin's equation

Pore diameter	Relative humidity	Method
1.0 nm	11%	Lithium chloride[2]
3.0 nm	48%	Water bath at 13.4°C
6.3 nm	71%	Water bath at 19.3°C
12.4 nm	84%	Potassium chloride[2]

\*As container temperature is 25°C

### 3.4 The experimental method

The pore volumes of prepared samples were measured by following the process given in Figure 3. The WVD measurements were carried out at the same time in containers with different relative humidity.

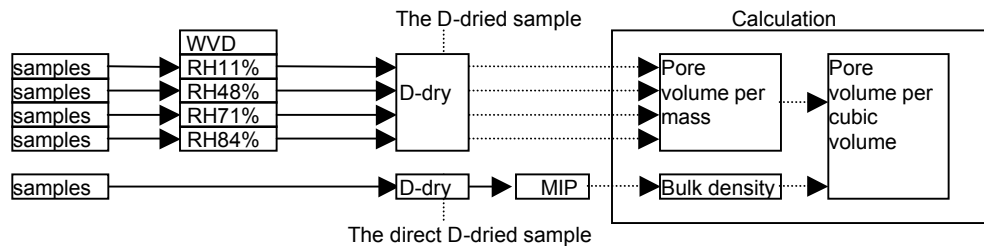


Figure 3. The WVD experimental method

### 3.5 Equilibrium of the water vapor desorption process

Each weighing bottle was placed in a container of different relative humidity. The weight loss of the sample was measured every three days. The rate of weight loss was calculated using equation (3). Equilibrium was judged to have been achieved when the rate of weight loss reached 0.03 %/24 h. Figure 4 shows an example of sample weight loss. Equilibrium was also judged to have been achieved for both the D-dried sample and the direct D-dried sample when the rate of weight loss reached 0.03 %/24 h.

$$\text{Rate of weight - loss} = \frac{W_{n-1} - W_n}{W_n} \times \frac{24}{t_n - t_{n-1}} \times 100 \text{ - Equation (3)}$$

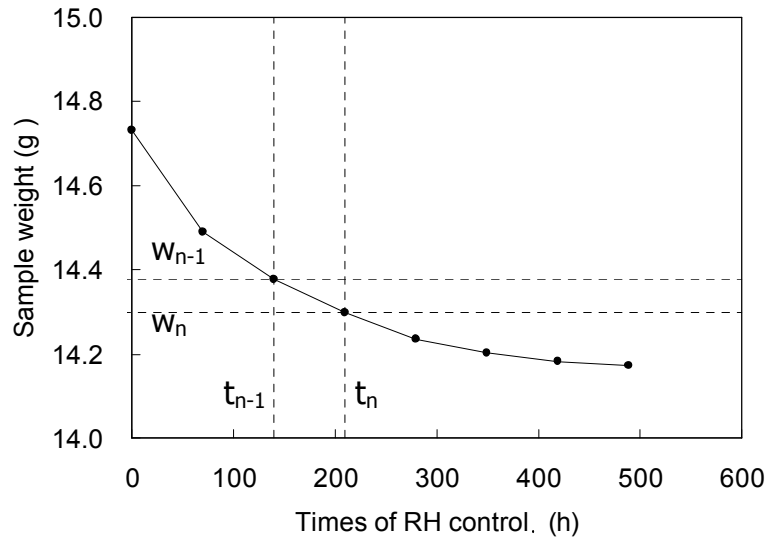


Figure 4. Example of sample weight loss  
[ordinary Portland cement, 7 days curing, RH11%]

### 3.6 The calculation of pore volume by WVD

The calculation of pore volume has the following five steps:

- (1) Calculation of condensed water

$$\text{CW-Mass (mg)} = (\text{RH-Mass (g)} - \text{D-Mass (g)}) \times 1000$$

- (2) Calculation of rate of condensed water in sample

$$\text{R-CW-Mass(W) (mg/g)} = \text{CW-Mass (mg)} / \text{D-Mass (g)}$$

- (3) Calculation of pore volume for mortar mass

Because the condensed water is in the pores and the water density is  $1\text{mg/mm}^3$ .

$$\text{PV (mm}^3/\text{g)} = \text{P-CW-Mass (mg)} / \text{water density (1mg/mm}^3\text{)}$$

- (4) Calculation of pore volume per cubic volume of D-dried mortar

$$\text{PV(V) (mm}^3/\text{cm}^3\text{)} = \text{PV(M) (mm}^3/\text{g)} \times \text{Bulk density (g/cm}^3\text{)}$$

- (5) Calculation of pore volume of a particular region per cubic volume of sample

Because the CW-Mass decreases between the D-dried and the chosen relative humidity, the pore volume at different relative humidity can be used to calculate each pore size region.

$$\text{Example: R-PV(6.3 -12.4 nm)} = \text{PV(V) of RH84\%} - \text{PV(V) of RH71\%}$$

Figure 5 shows an illustration of pore volumes.

CW-Mass: mass of condensed water

RH-Mass: mass of sample that has reached equilibrium for the water vapor desorption process

D-Mass: mass of sample that has reached equilibrium for the D-dry process

R-CW-Mass: rate of condensed water in D-dried sample

PV(M): pore volume per mass of D-dried sample

PV(V): pore volume per cubic volume of D-dried sample

Bulk density: bulk density of D-dried mortar estimated by MIP

R-PV(region) : pore volume per cubic volume for a certain region

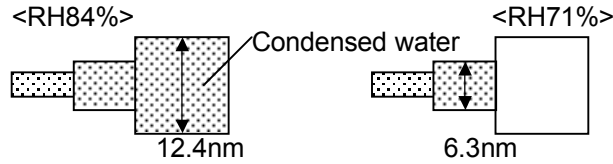


Figure 5. An illustration of pore volumes

Fujii [3] found that the  $H_2O/CaO$  of C-S-H was 1.54. Also Taylor [4] reviewed the  $H_2O/CaO$  of C-S-H was 1.20 at RH11%. Thus, we assumed that bound water of C-S-H almost remains at RH11% and we calculated pore volumes by WVD on the basis of the assumption.

### 3.7 Mercury intrusion porosimetry (MIP)

The direct D-dried samples were analyzed by MIP. The basic constants used for calculation were as follows: the surface tension of mercury was 0.483 N/m, the contact angle of mercury was 130 degree, and the density of mercury was calculated at room temperature.

Bulk density was estimated by the mercury method.

### 3.8 Thermal analysis

The direct D-dried samples and the D-dried samples were ground to 105  $\mu m$ . The samples were analyzed by TG-DTA with a 20°C/min rate of temperature in a nitrogen atmosphere.

## 4. RESULTS AND DISCUSSION

### 4.1 Time taken to reach water vapor desorption equilibrium

Table 6 shows the time taken to reach water vapor desorption equilibrium. The longest time taken to reach equilibrium was about one month. The D-dried sample took about two weeks to reach equilibrium.

Table 6. Time(days) taken to reach water vapor desorption equilibrium

	Curing days	RH11%	RH48%	RH71%	RH84%
H	3	21	21	24	6
	7	21	28	24	9
	28	18	24	18	3
O	3	21	21	27	9
	7	21	28	24	9
	28	18	24	15	6
M	3	18	21	15	9
	7	21	24	24	15
	28	18	24	18	6
L	3				
	7	15	15	15	12
	28	18	27	18	3

#### 4.2 Effect of progress of hydration and carbonation on the water vapor desorption process

Table 7 shows the amount of calcium hydroxide measured by TG-DTA. During the water vapor desorption process hydration did not progress very far. Also, using TG-DTA, the carbon dioxide peaks in calcium carbonate were not observed at about 780°C.

Table 7. Amount of calcium hydroxide (%) measured using TG-DTA

[H]				[O]			
	3days	7days	28days		3days	7days	28days
D-dry	3.86	4.44	5.04	D-dry	2.57	3.92	4.68
RH48%	4.01	4.48		RH48%	3.10	3.80	
RH84%	4.14	4.12		RH84%	2.99	3.95	

[M]				[L]			
	3days	7days	28days		3days	7days	28days
D-dry	2.24	2.96	3.73	D-dry		1.21	2.01
RH48%	2.58	3.08		RH48%		1.16	
RH84%	2.46	3.19		RH84%		1.23	

#### 4.3 Porosimetry by WVD and MIP

Table 8 shows the pore volumes calculated by WVD.

Figure 6 shows the relationship between measurement by WVD and MIP and pore volume for pores between 6.3 and 12.4 nm in diameter. The pore volume measured by WVD was larger than by MIP. Figure 7 shows the integrated pore size distributions from 6.3 nm to 10 μm measured by MIP and also the integrated pore size distributions smaller than 12.4 nm measured by WVD.

Table 8. Pore volume using WVD (mm<sup>3</sup>/cm<sup>3</sup>)

cement	Curing days	1.0-3.0nm	3.0-6.3nm	6.3-12.4nm	1.0-12.4nm
H	3days	29.62	16.42	29.14	75.18
	7days	27.92	25.41	33.92	87.25
	28days	34.77	19.87	23.38	78.02
O	3days	26.45	18.41	14.44	59.30
	7days	27.85	27.30	22.70	77.85
	28days	40.43	20.93	16.45	77.81
M	3days	21.57	15.61	15.72	52.90
	7days	24.26	19.79	24.97	69.02
	28days	33.47	22.92	24.81	81.20
L	3days				
	7days	20.18	9.59	9.87	39.64
	28days	35.87	20.26	20.30	76.43

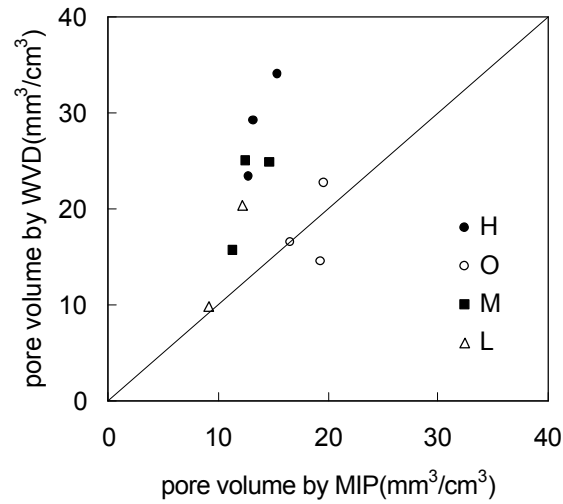


Figure 6. Pore volumes measured by WVD and MIP

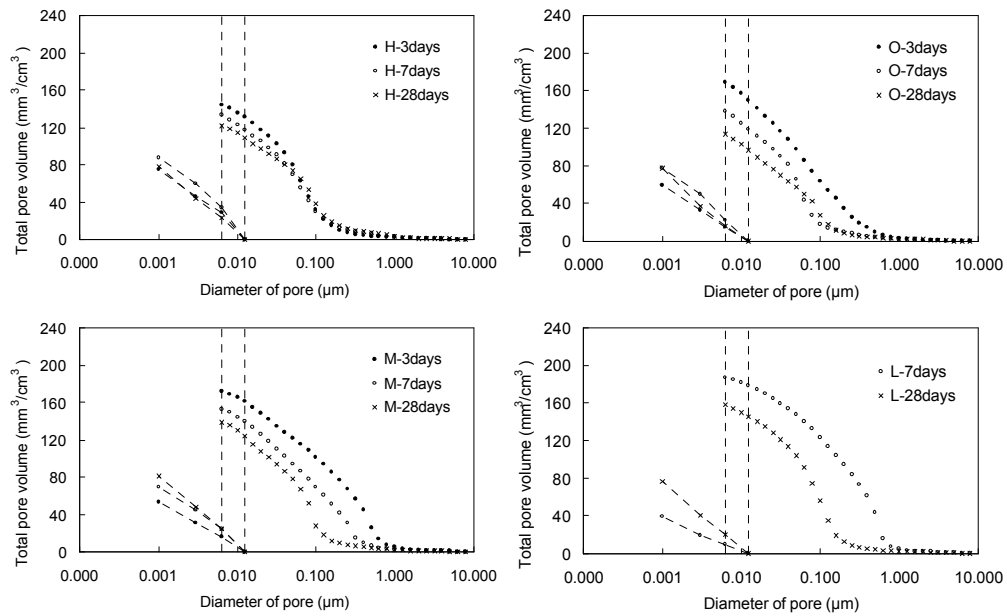


Figure 7. Integrated pore size distributions measured by MIP and WVD

#### 4.4 Hydration model

It is generally thought that the hydration reaction of the calcium silicate phases barely changes the volume. Thus Figure 8 shows a model of hydration of the calcium silicate phase.



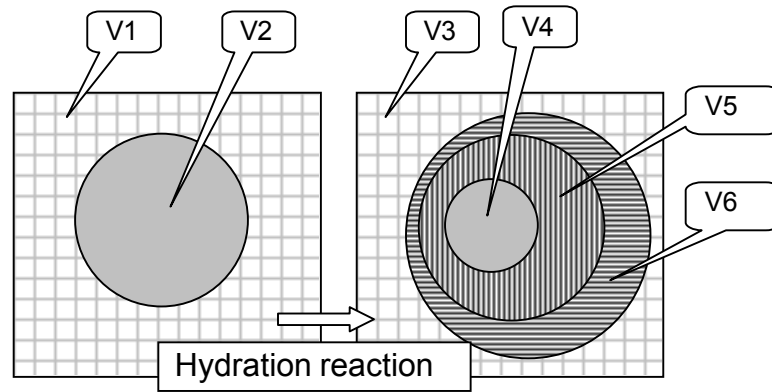


Figure 8. Hydration reaction model of calcium silicate phases (V1 or V3= water, V2 or V4=anhydrous calcium silicate phases, V5 or V6= C-S-H with calcium hydroxide)

#### 4.5 Relationship between the amount of calcium hydroxide and the pore volumes of each region

According to the hydration reaction model, when the amount of calcium hydroxide increases by hydration of the calcium silicate phases, the number of pores in the C-S-H also increases. The correlation coefficients between pore volumes of several regions with pores larger than 1.0 nm and the amount of calcium hydroxide are shown in Table 9. High early strength Portland cement and ordinary Portland cement cured for 28 days were excluded because of different trends. In Table 9, the correlation coefficient was high between 1.0 and 12.4 nm. Figure 9 shows the relationship between the amount of calcium hydroxide and pore volumes for several cements in the 1.0 -12.4 nm pore diameter range. It is suggested that the 1.0 -12.4 nm diameter pores are in the C-S-H.

Table 9. Correlation coefficients between pore volumes of several regions and the amount of calcium hydroxide

Region(nm)	H	O	M	L
1.0-3.0	-	-	0.954	0.995
1.0-6.3	0.998	-	0.972	0.983
1.0-12.4	0.998	0.850	0.975	0.978

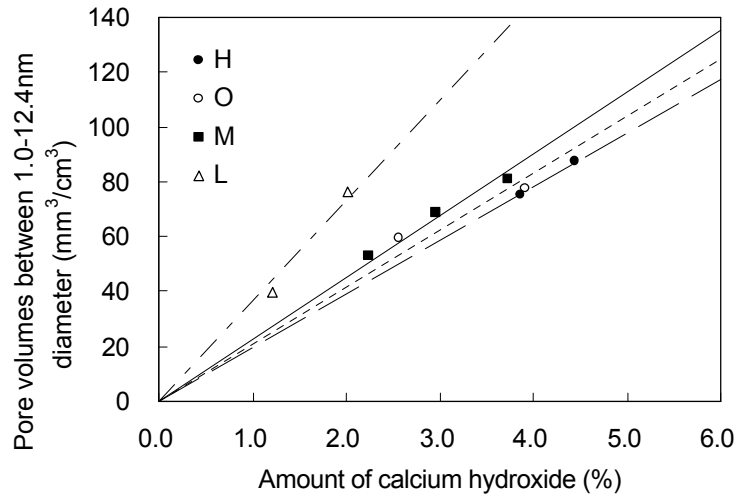


Figure 9. Relationship between amount of calcium hydroxide and pore volumes between 1.0 and 12.4 nm pore diameter

#### 4.6 Relationship between capillary pore volume and compressive strength

If the pore size diameter in the C-S-H is assumed to be in the range 1.0 - 12.4 nm, capillary pores larger than 12.4 nm in diameter would be defects in the structure of the hardened cement. Thus, if the capillary pore volume is low, it is possible for the compressive strength to be strong. Figure 10 shows the relationship between capillary pore volume for 12.4 nm - 10 μm diameter pores and compressive strength. In Figure 10, each type of cement has a different relative line. When moderate and low heat Portland cement are compared with ordinary Portland cement, although the pore volume is larger, the compressive strength tends to be stronger.

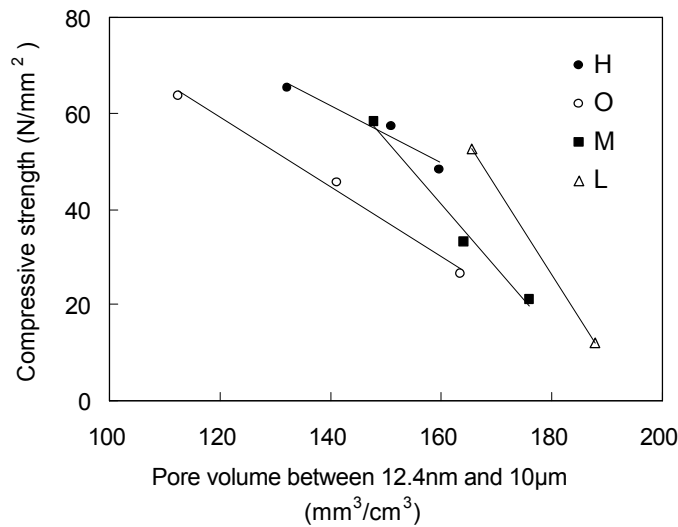


Figure 10. Relationship between capillary pore volume and compressive strength for several cement mortars

## **5. CONCLUSIONS**

- (1) About six weeks was needed to measure pore volume by WVD.
- (2) During the desorption experiment, hydration did not progress very far.
- (3) A larger pore volume was measured by WVD than by MIP.
- (4) Pore volumes between 1.0 and 12.4 nm diameter correlated with the amount of calcium hydroxide.
- (5) With regard to the relationship between pore volume and compressive strength, in the 12.4 nm-10  $\mu$ m diameter range, each type of cement had a different relative line.

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