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Hydration of cement and pore structure of concrete cured in tropical environment

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Abstract

This paper presents the results of an experimental study on the effect of curing on the degree of cement hydration and capillary porosity of concrete in a tropical environment. It provides basic information for the estimation of w/c of hardened concrete using petrographic methods. Concrete with w/c ratios of 0.30 to 0.70 with an increment of 0.05 was investigated. The concrete was cured at 20 and 35 °C and exposed to various durations of moist curing. The results indicated that the concrete cured at 20 °C water for 28 days had a higher degree of cement hydration and lower capillary porosity than did the concrete cured in water of the same temperature for 7 days followed by exposure to outdoor air for 21 days, but had an opposite trend compared to the concrete cured in 35 °C water for 7 days followed by exposure to outdoor air. However, the differences on the degree of cement hydration and capillary porosity for the concrete cured in these different conditions were not significant.

Keywords: Pore size distribution; Curing; Hydration; Temperature; w/c ratio

1. Introduction

Petrography has been used for research and forensic investigation of concrete in Europe and North America for many years. Most of the information available is based on cement pastes and concretes cured at a standard temperature of ~20 °C. However, many South East Asian countries are located near the equator, and the temperature and humidity are relatively high. For example, the temperature in Singapore ranges from ~23 °C at night to ~33 °C during the day, and the relative humidity (RH) ranges from ~65% to 95%, with a daily average of 84% throughout the year. As the weather conditions of the South East Asian countries are quite different from those from Europe and North America, study is needed to assess if the petrographic methods can be used to determine the water-to-cement ratio (w/c) and cement content of concrete cured in tropical environment, and if any adjustment is needed.

In the petrographic methods developed [1–6], the estimations of w/c using fluorescent thin section and cement content of hardened concrete are essentially based on the capillary porosity, degree of cement hydration, quantity of unhydrated cement particles, density and volume of cement paste, or a combination of the above. Since the capillary porosity, degree of cement hydration, and quantity of unhydrated cement clinker are affected by the curing conditions substantially, the effect of curing on these parameters must be known to estimate the w/c and cement content accurately.

This paper presents the results of an experimental study on the effect of curing on the degree of cement hydration and capillary porosity of concrete. Concrete with w/c ratios of 0.30 to 0.70 with an increment of 0.05 was investigated. The concrete was cured at 20 and 35 °C and exposed to various durations of moist curing. Compressive strength, degree of cement hydration, capillary porosity, and pore size distribu-

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tion were determined. The results will be used for the estimation of w/c and cement content of hardened concrete by petrographic methods, which are reported elsewhere [7].

2. Experimental

2.1. Materials

Ordinary Portland cement (ASTM Type I), natural sand, and crushed granite with maximum size of 20 mm were used for all concrete mixes. Chemical admixtures were also used, and the information is given together with the concrete mix proportions (Table 1).

2.2. Concrete mix proportions and curing conditions

Concrete with w/c ratios of 0.30 to 0.70 with an increment of 0.05 was prepared and cured at 35 °C and 20 °C, respectively. Cubes of 100 mm and prisms of 100×100×500 mm were cast from each concrete mix. The mix proportion and properties of the fresh concrete are presented in Table 1. After 24 h curing in moulds covered with plastic sheet, the specimens were demoulded and cured under the following conditions:

Series 1: 20 °C, 6 additional days in water followed by 21 days in air outside the lab (sheltered).
Series 2: 20 °C, 27 additional days in water followed by 28 days in air outside the lab (sheltered), and
Series 3: 35 °C, 6 additional days in water followed by 21 days in air outside the lab (sheltered).

As mentioned earlier, the temperature in Singapore ranges from ~23 °C at night to ~33 °C during the day. Because it is a tropical country, the change in the daily temperature throughout a year is relatively small. The two temperatures of 20 and 35 °C were selected to simulate the low and high temperatures in Singapore. It should be noted that the outdoor temperatures were not exactly 20 or 35 °C. In Singapore, 7-day moist curing was commonly specified in practice. Thus 7-day moist curing was selected for Series 1 and Series 3. Although the specification may not be followed strictly at jobsites, moist curing period shorter than 7 days is less critical in Singapore compared with in many other countries. This is due to its high relative humidity (RH) with mean daily maximum of ~95% to 97% and mean daily minimum of ~61% to 68%.

Some concrete specimens were also cured in water continuously up to 56 days for determining the compressive strength and the degree of cement hydration for control purposes.

2.3. Experimental methods

The compressive strength, degree of cement hydration, and capillary porosity of the concrete were determined at various ages. The pore structure of the mortar in the concrete was also determined using mercury intrusion porosimetry (MIP).

Table 1
Mix proportion of concrete

Mix ID	Design W/c	Temperature of initial water curing (°C)	Materials (kg/m^3)					
			Cement	Fine aggregate	Coarse aggregate	Water	Admixture 1 Dosage (kg/m^3)	Admixture 2 Dosage (kg/m^3)
1	0.70	20	275	911	911	192	2.72[a]	–
		35					2.72[a]	–
2	0.65	20	300	866	935	195	2.31[a]	–
		35					2.31[a]	–
3	0.60	20	325	823	967	195	1.50[b]	–
		35					1.95[b]	–
4	0.55	20	350	782	996	192	1.2[b]	–
		35					2.3[b]	–
5	0.50	20	375	747	1031	187	1.35[b]	–
		35					2.70[b]	–
6	0.45	20	400	712	1068	180	1.48[b]	–
		35					3.12[b]	–
7	0.40	20	425	678	1107	170	4.48[b]	–
		35					5.10[b]	–
8	0.35	20	450	645	1148	157	1.89[c]	1.05[d]
		35					3.07[c]	1.05[d]
9	0.30	20	475	613	1190	142	6.28[c]	1.05[d]
		35					6.98[c]	1.11[d]

[a] A lignosulfonate based water-reducing admixture.
[b] A sodium naphthalene sulfonates/lignosulfonate based retarding high-range water reducing admixture.
[c] A polycarboxylate based superplasticizer.
[d] A hydroxycarboxylic acid salts based retarder.

2.3.1. Compressive strength

The compressive strength of the concrete was determined according to the BS 1881 Pt. 116 [8] at 1, 7, 28, and 56 days. Three cubes were used for each testing age and the average values were calculated and presented.

2.3.2. Degree of cement hydration

The degree of cement hydration of the concrete was determined in accordance with the ASTM C 1084: 1997 [9] and Adnan et al. [10]. In this method, the non-evaporated water content Wn was used to evaluate the degree of hydration. The degree of hydration was estimated by the following:

$$\alpha = \mathrm{Wn}/\mathrm{Wnu} \tag{1}$$

where Wnu is the nonevaporable water content at complete hydration which is taken to be 0.23 g/g of cement ([11], Concrete Society 1989).

After the compressive strengths test, one out of the three crushed concrete cubes from each curing age was chosen randomly for the determination of the non-evaporable water content. The cube was cut vertically into slices of approximately 15-mm thick and immersed in methanol to stop cement hydration. The specimen was then dried at 105±1 °C and ground into fine particles (passing 1.18-mm sieve). A sample of approximately 10 g was used and ignited at 520±5 °C for 3 h. The nonevaporable water content Wn per gram of cement was determined from Eq. (3).

$$\mathrm{Wn} = (W_1 - W_2)/(W_2 \times C_{\mathrm{cem}}) \tag{2}$$

where W_1—oven-dried weight of the sample; W_2—weight after ignition; and C_{cem}—percentage cement content in concrete.

The degree of cement hydrated in the concrete was then calculated by Eq. (2).

2.3.3. Capillary porosity and pore structure

2.3.3.1. Capillary porosity determined according to BS 1881 Pt. 124:1988. The capillary porosity of the concrete is a main concern for the w/c analysis by fluorescence microscopy and was determined by the BS 1881 Pt. 124 [12]. In this test, two slices of concrete each approximately 20-mm thick were cut vertically from the mid-length of the concrete beams, which had been cast from concrete mixes with w/c ratios of 0.30, 0.40, 0.50, 0.60 and 0.70 for all the three curing conditions given in Section 2.2. The surfaces of the samples were washed and cleaned before they were dried in an oven at 105±1 °C until the constant weight was reached. They were then transferred to a vacuum desiccator and vacuumed under a pressure of 30 mm Hg (4 kPa) for 4 h. Xylene was then introduced through a funnel with the vacuum pump running until the samples were fully covered by the xylene. The xylene impregnation was carried out until no air bubble came out of the concrete samples, and this took approximately 8 h. The pressure was then released and the samples were kept in the xylene for an additional 5 min at atmospheric pressure. The samples were surface dried and weighed. The average values of the results from two samples were used for data comparison.

2.3.3.2. Capillary porosity and pore structure determined by mercury intrusion porosimetry. The pore structure of the mortar in concrete was determined by a mercury intrusion porosimeter (Carlo Erba POROSIMETER 4000). In this method, mercury is forced into the pores of the sample under applied pressures. Pore size is related to the pressure by the Washburn's equation, which assumes that the pores have circular cross sections:

$$P = \frac{-2\sigma' \cos\theta}{r} \tag{3}$$

where P—pressure exerted (N/m^2); r—the pore radius (Å); σ' —surface tension of mercury (N/m), and θ—contact angle (°).

In this study, a maximum pressure of 3×10^8 N/m^2 was applied. The surface tension (σ') of 0.480 N/m and the contact angle (θ) of 141.3° were used for the calculation of pore size.

Two to four millimeters of mortar, approximately 50 g of samples, were chiseled carefully from the mid-length of the concrete beams, which had been cast from concrete mixes with w/c ratios of 0.30, 0.50, and 0.70 for all the three curing conditions given in Section 2.2. These mortar samples then were soaked in acetone and oven-dried at 105±1°C to constant weight. The samples were then kept in a vacuum desiccator before testing. Two MIP tests were conducted for each sample, and the average values of the MIP results were used for data comparison.

Mercury intrusion porosimetry provides the pore size distribution of the samples for relative comparison. The capillary porosity was obtained from the MIP results for pores >~10 nm. The inflection point from the curve of volume versus size of the pores (or the maximum of the dV/dp curve) was taken to be the critical pore diameter. Katz and Thompson [13] suggested that this point corresponds to the smallest pore size that creates connected paths through the sample. The MIP test results of the mortars were converted to those of the concrete based on the mix proportions of the concrete.

3. Results and discussion

3.1. Degree of cement hydration and compressive strength of concrete

The compressive strength of the concrete and the corresponding degree of cement hydration are shown in

Table 2
Compressive strength of concrete and the corresponding degree of cement hydration (temperature of water curing=20 °C)

W/C	Compressive strength (MPa)						Degree of cement hydration					
	1-day	7-day	28-day	28-day[a]	56-day	56-day[b]	1-day	7-day	28-day	28-day[a]	56-day	56-day[b]
0.70	2.7	17.4	25.8	26.4	28.2	33.8	0.34	0.71	0.83	0.81	0.86	0.82
0.65	4.3	21.7	32.1	35.1	35.3	39.4	0.33	0.69	0.79	0.78	0.81	0.78
0.60	6.1	26.9	34.6	33.5	36.7	42.5	0.31	0.67	0.71	0.71	0.75	0.73
0.55	8.2	31.4	42.3	44.3	47.9	52.5	0.30	0.65	0.70	0.68	0.72	0.69
0.50	10.8	37.8	50.2	52.2	56.3	61.5	0.28	0.63	0.67	0.65	0.69	0.65
0.45	12.6	41.6	58.9	59.9	62.5	66.8	0.27	0.61	0.64	0.63	0.65	0.63
0.40	16.2	53.9	63.1	65.0	70.6	74.4	0.25	0.56	0.60	0.57	0.61	0.59
0.35	20.8	68.3	81.9	83.2	86.3	89.1	0.23	0.51	0.57	0.56	0.59	0.57
0.30	24.0	76.5	89.8	92.0	97.7	99.1	0.20	0.50	0.55	0.54	0.58	0.54

[a] Concrete cured in water for 7 days and left outside the lab for another 21 days.
[b] Concrete cured in water for 28 days and left outside the lab for another 28 days.

Tables 2 and 3. As expected, the degree of cement hydration increased with time and temperature. The results also show that after water curing at 20 °C for 28 days, the degree of cement hydration increased somewhat if the concrete was continuously cured in water for another 28 days, but did not change significantly if the concrete was left in air outside the lab for the same period.

The degree of cement hydration in concrete cured at 20 °C in water for 28 days was slightly lower than that cured in 35 °C water for 7 days followed by 21 days in outdoor air, but similar to or slightly higher than that cured in 20 °C water for 7 days followed by 21 days in outdoor air. However, the differences were not significant. The results can be explained by the curing conditions and high relative humidity in Singapore mentioned earlier. This suggests that the reference thin sections of concrete cured at 20 °C in moist condition for 28 days may be used to estimate the w/c of concrete cured in the condition typical in tropical environment without determining the degree of cement hydration of the concrete under investigation.

The results from the compressive strength showed the similar trend as the degrees of cement hydration.

It should be noted that for concrete elements with relatively low surface/volume ratios (mass concrete), the temperature and humidity of the interior concrete are generally higher than those near surface. Therefore, the degree of hydration of the interior concrete may be higher than that near surface.

3.2. Porosity

3.2.1. Capillary porosity determined by BS 1881: Pt 124:1988

The capillary porosity of the concrete determined according to BS 1881 Pt. 124 [12] and that calculated are shown in Table 4. The calculated capillary porosity of concrete was obtained by the calculated capillary porosity of cement paste according to Eq. (4) [14] multiplied by the percentage of cement paste volume in the concrete calculated based on the mix design and the measured air content.

$$P = \frac{w/c - 0.36\alpha}{w/c + 0.32} \tag{4}$$

where P is the capillary porosity and α is the degree of cement hydration.

As expected, the capillary porosity decreased with the w/c. The results also showed that at 20 °C, the capillary porosity of

Table 3
Compressive strength of concrete and the corresponding degree of cement hydration (temperature of water curing=35 °C)

W/C	Compressive strength (MPa)					Degree of cement hydration				
	1-day	7-day	28-day	28-day [a]	56-day	1-day	7-day	28-day	28-day[a]	56-day
0.70	8.3	29.5	31.4	36.5	38.3	0.65	0.80	0.89	0.85	0.91
0.65	11.2	31.5	38.3	39.8	39.5	0.63	0.78	0.86	0.82	0.87
0.60	16.2	36.5	43.6	44.0	43.4	0.62	0.72	0.82	0.76	0.82
0.55	17.7	46.9	48.9	52.0	48.9	0.60	0.70	0.74	0.72	0.75
0.50	19.1	49.7	58.0	60.0	59.5	0.59	0.67	0.72	0.70	0.73
0.45	24.2	53.6	62.0	66.5	61.6	0.58	0.64	0.68	0.65	0.68
0.40	26.7	61.8	67.5	72.6	70.2	0.53	0.60	0.63	0.62	0.65
0.35	29.8	75.4	85.7	91.0	90.7	0.44	0.58	0.63	0.61	0.64
0.30	42.8	88.6	95.1	101.0	106.0	0.44	0.56	0.60	0.58	0.61

[a] Concrete cured in water for 7 days and left outside the lab for another 21 days.

Table 4
Porosity of concrete determined by mercury intrusion porosimetry and calculated capillary porosity

Curing condition			w/c	BS 1881 capillary porosity (%)	Calculated capillary porosity (%)	MIP results for concrete		
Temperature of water curing (°C)	Length of water curing (days)	Length of outside exposure (days)				Capillary porosity (%)	Critical diameter (μm)	Total porosity (%)
20	7	21	0.70	6.8	10.2	14.7	0.422	18.5
20		–	0.70	6.8	10.0	13.7	0.344	18.2
35	7	21	0.70	7.0	10.2	10.8	0.300	15.1
20	7	21	0.60	6.1	11.4	–	–	–
20	28	–	0.60	6.1	11.1	–	–	–
35	7	21	0.60	5.7	10.2	–	–	–
20	7	21	0.50	5.1	9.5	11.6	0.150	14.4
20	28	–	0.50	5.3	9.6	10.7	0.076	14.4
35	7	21	0.50	4.5	9.1	9.4	0.106	12.5
20	7	21	0.40	4.5	7.6	–	–	–
20	28	–	0.40	4.1	7.5	–	–	–
35	7	21	0.40	4.2	7.4	–	–	–
20	7	21	0.30	3.6	5.0	6.8	0.076	9.0
20	28	–	0.30	3.2	4.8	6.1	0.054	8.1
35	7	21	0.30	3.0	4.3	4.9	0.054	7.3

concrete cured in water for 28 days was not significantly different from that of the concrete cured in 20 °C water for 7 days followed by exposure in outdoor air for 21 days. This is probably related to the high humidity in the tropical environment so that the cement could continue to hydrate even when the concrete was exposed to outdoor air. Besides, the temperature outside the lab was higher than 20 °C; this partly compensated for the lower degree of cement hydration for the concrete exposed in air compared to that in water. However, concrete cured at 35 °C appears to have somewhat lower capillary porosity than the concretes cured at 20 °C for 7 days in water followed by 21 days in outdoor air, with some exceptions.

The capillary porosity determined according to BS 1881 showed lower values than the calculated one. This might be due to the incomplete penetration of xylene into the concrete samples in the determination of the capillary porosity by the BS 1881 method, and due to the lower degree of cement hydration that was determined according to the ASTM C1084 at 520 °C and used for the calculation of capillary porosity. The lower degree of hydration resulted in higher calculated capillary porosity.

3.2.2. *Capillary porosity determined by mercury intrusion porosimetry*

The total porosity, critical diameter, and the capillary pores calculated based on the MIP test results are presented in Table 4, and the pore size distribution curves are presented in Figs. 1–6. The capillary pores included pores with sizes from 0.01 to 10 μm (100–100,000 Å). In terms of the effect of w/c and curing on the porosity, a similar trend to that of the porosity determined by BS 1881 method was observed.

The test results from MIP shows that the capillary porosity and critical diameter of concrete decreases with the

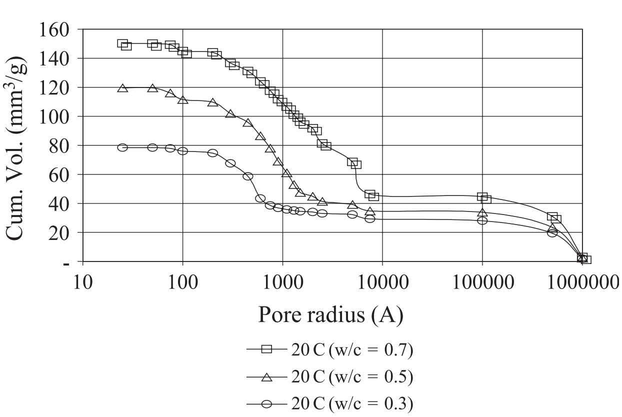

Fig. 1. Effect of w/c on the pore size distribution of mortar in concrete cured in 20 °C water for 7 days followed by exposure in air for 21 days.

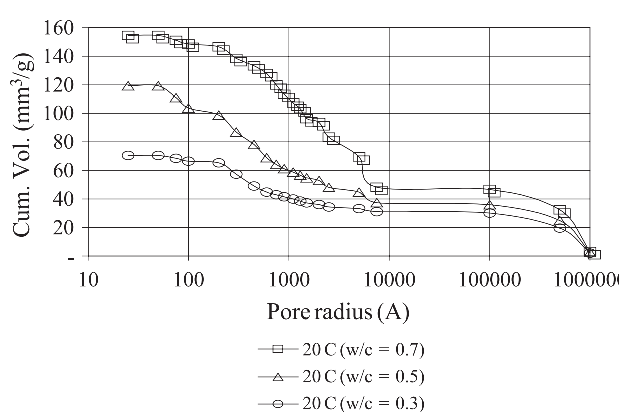

Fig. 2. Effect of w/c on the pore size distribution of mortar in concrete cured in 20 °C water for 28 days.

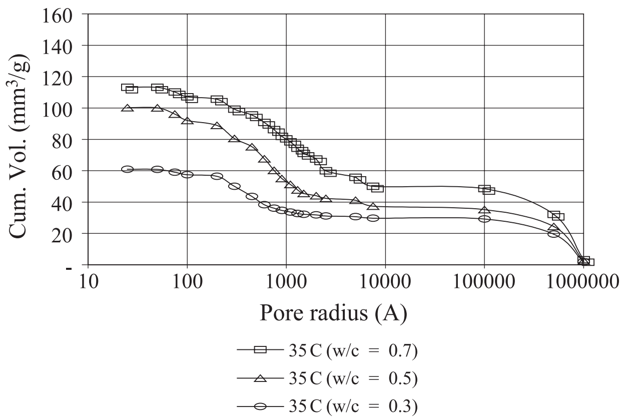

Fig. 3. Effect of w/c on the pore size distribution of mortar in concrete cured in 35 °C water for 7 days followed by exposure in air for 21 days.

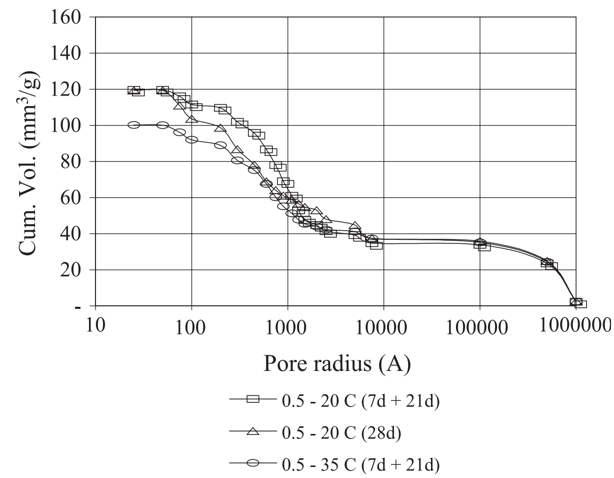

Fig. 5. Effect of curing conditions on the pore size distribution of mortar in concrete with w/c=0.5.

w/c. The capillary porosity of concrete cured in 20 °C water for 28 days was slightly lower than that of the concrete cured in 20 °C water for 7 days followed by exposure in outdoor air for 21 days. However, it appears to have higher capillary porosity than the concrete cured in 35 °C water for 7 days followed by exposure in outdoor air for 21 days. This was consistent with the results on the cement hydration shown in Tables 2 and 3.

The total porosity determined by the MIP was higher than that determined by BS 1881 Pt. 124 method. This could be due to: (a) the porosity determined by the MIP method included the small capillary pores down to ~10 nm (100 Å) according to the definition by Mindess and Young [14], whereas that determined by the BS 1881 method included probably the relatively large capillary pores; (b) the method for the preparation of the samples for the MIP test may have impacted on the porosity values; for example, mechanically chipping mortar from the concrete beams and subsequent drying might have created microcracks in the samples; (c) high pressures of the mercury in the test might have damaged the pore structure.

The results from the MIP in this study show that the pore size distribution of the mortar in the concrete was affected not only by the w/c, but also by the curing conditions. However, the differences due to the w/c ratio seem to be greater than the differences due to the curing conditions.

It should be noted that the different test methods for the determination of capillary porosity yield different results for the same concrete, and this might be attributed to the suitability and limitation of each test method. The test results from BS 1881 may be more reliable than the test results from MIP, as the MIP test could be affected by many factors. According to Diamond [15], conditions that must be met for MIP measurements to provide valid estimates of pore size distribution of porous solids are not satisfied in cement-based systems. He suggests that the method should not be used to measure the actual pore size distribution but

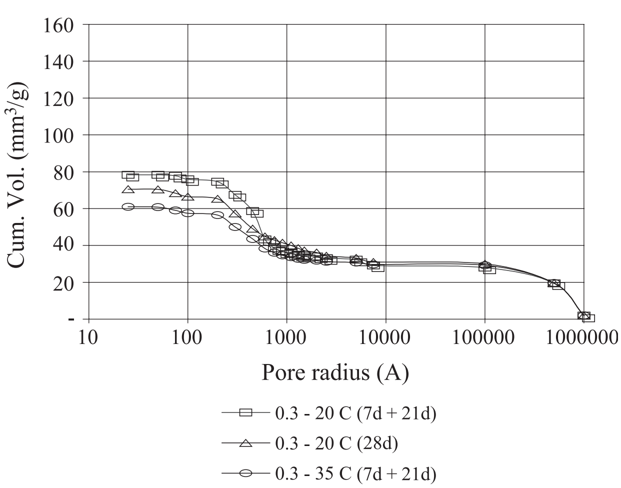

Fig. 4. Effect of curing conditions on the pore size distribution of mortar in concrete with w/c=0.3.

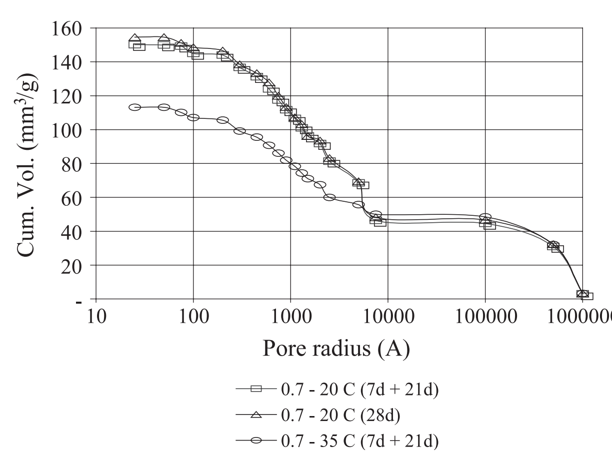

Fig. 6. Effect of curing conditions on the pore size distribution of mortar in concrete with w/c=0.7.

only to provide threshold diameters and porosity for comparison purposes.

4. Conclusions

Based on the limited results available, the following conclusions may be drawn:

(1) The degree of cement hydration increased with time and temperature, but the increase beyond 28 days was not significant.
(2) The concrete cured at 20 °C water for 28 days had a higher degree of cement hydration and lower capillary porosity than the concrete cured in water of the same temperature for 7 days followed by exposure to outdoor air for 21 days, but had opposite trend compared to the concrete cured in 35 °C water for 7 days followed by exposure to outdoor air. However, the differences on the degree of cement hydration and capillary porosity for the concrete cured in these different conditions were not significant. This suggests that the reference thin sections of concrete cured at 20 °C in moist condition for 28 days may be used to estimate the w/c of concrete cured in a tropical environment for at least 28 days, including 7 days moist curing without the need to determine the degree of cement hydration of concrete under investigation.

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