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Influence of superplasticizer and curing on porosity and pore structure of cement paste ☆

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Abstract

Most concrete produced today contains admixtures. Superplasticizers (SP) are used for the purpose of improving workability and reducing the water to cement ratio; therefore producing more durable concrete. SP cause better dispersion even at high water to cement ratio. Although SP improves the dispersion of particles, it is not quite clear how the addition of SP affect the porosity and pore size distribution of cement paste. The purpose of this study was to examine the influence of one type of SP on porosity and pore size distribution under different curing regimes. Paste specimens with and without SP were prepared at constant water to cement ratio of 0.45. Specimens were cured for 28 days and some for six months. Specimens were exposed to high temperature (45°C) and normal temperature curing (20°C) and also subjected to different relative humidities (~100%, 55% and 25%). Curing at high temperature was carried out to simulate temperature in hot climates. Tests on porosity and pore size distribution were conducted using mercury intrusion porosimetry. The results show that the inclusion of SP decreases the total intruded pore volume of paste. The dominant pore diameter, however, does not seem to be affected and the percentage of pores smaller than 100 nm increases in the presence of SP. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Curing; Pore size distribution; Pore volume; Superplasticizer

1. Introduction

The presence of superplasticizers (SP) in a concrete mixture is quite advantageous, in that they assist in the effective dispersion of cement particles and hence improving the workability of concrete [1]. The water to cement ratio is reduced when SP is added to cement paste, which leads to reduced permeability, increased strength and producing durable concrete [2]. SP are broadly classified into four groups, sulphonated melamine-formaldeyde condensate (SMF), sulphonated naphthalene-formaldehyde condensate (SNF), modified lignosulphonates (MLS) and others including sulphonic-acid esters and acrylic esters [3,4].

At a constant water to cement ratio, the addition of SP is variously reported to increase, to decrease or to have no influence on the porosity of cement paste, mortar or concrete [5–12], but many have agreed that a refinement of the pore structure is obtained in the presence of SP [5,7,12]. The rate of hydration was reported to increase when SP is included [11], while others reported a retardation in cement hydration [9,10]. Table 1 presents the data on porosity, pore structure and hydration which were obtained by different workers [5,6,8,10–12]. Apparently it is not clear on how the addition of SP affects the porosity, pore structure or hydration of cement paste. The strength of concrete was reported to increase in the presence of SP [12–15]. An optimum dosage level of about 2.0–2.5% of SP was found to give a maximum value of strength, beyond which level the strength begins to decline [13,14], which indicates that the rate of hydration increases when SP is present in the system (paste, mortar or concrete) up to an optimum dosage of between 2% and 2.5%. However, others [16] reported that an increase in strength was obtained up to an SP dosage level of about 1% (by mass of cement). Beyond this level (i.e. 1%) a decline in compressive strength was observed.

The aim of the present work is to further examine the influence of SP addition on porosity and pore structure of cement paste at a constant water to cement ratio. The cement pastes were subjected to different curing temperatures (i.e. high temperature and normal tempera-

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Table 1
Influence of SP addition on porosity and pore structure for data obtained by different workers

Year	Ref No.	SP type	SP dosage[a] (%)	*W*/*C*	Age	Pore volume	Pore structure	Hydration
1984	[5]	SMF or SNF	1	0.28	28 d	Increased	Refined	Accelerated
1986	[7]	SNF		0.35	365 d	Decreased	Refined	
1990	[6]			0.5	112 d	No change		
1992	[10]	SMF	0.5	0.5	90	Decreased	Refined	Retarded
1992	[10]	SNF	0.5	0.5	90	Increased	Coarsened	Retarded
1994	[9]	SMF or SNF	1.5	0.3	1–28 d	Increased	Coarsened	Retarded
1995	[11]	SMF	4	0.28	1–3 yr	Decreased		Accelerated

[a] Percent by mass of cement.

ture) and different relative humidities (high and low). Only one type and one dosage of SP were used in this investigation.

2. Experimental programme

2.1. Materials

Ordinary Portland cement was used, the composition of which is given in Table 2. The water used was distilled. The water to cement ratio (*W*/*C*) was kept constant at 0.45. Pastes with and without SP were prepared. The dosage of SP was 1.2% by mass of cement. The SP was the sodium salt of a sulphonated napthalene-formaldehyde condensate. The SP conformed to Types F and G of ASTM C 494. The main features of the SP used are listed in Table 3.

Table 2
Composition of the cement

SiO_2 (%)	20.4
Al_2O_3 (%)	4.89
Fe_2O_3 (%)	3.18
CaO (%)	64.02
MgO (%)	2.56
SO_3 (%)	2.85
Na_2O (%)	0.07
K_2O (%)	0.53
Insoluble residue (%)	0.37
Loss on ignition (%)	0.98
Free lime (%)	2.37
C_3S (%)	47.82
C_2S (%)	23.14
C_3A (%)	7.56
C_4AF (%)	9.69
Specific surface area (m^2/kg)	367.76
Residue retained on 45 μm sieve (%)	15.16
Initial set (min)	84.20
Final set (min)	136.50

Table 3
Properties of superplasticizer

Specific gravity	1.08 at 20°C
Viscosity	Approx. 8cP
Air entrainment	Nil
Chloride content	Nil
Freezing point	−17°C
Ash content	9%
Appearence	Dark brown liquid

2.2. Curing

Cube specimens ($100 \times 100 \times 100$ mm^3) were cast in steel moulds. Five different curing regimes were adopted. Specimens were subjected to high temperature (to simulate temperature in hot climates) and normal temperature. Details of the curing methods are described below and given in Table 4.

1. After casting, specimens in their moulds were subjected to air curing at 45°C and 25% R.H. After demoulding specimens continued to be cured in air at 45°C and 25% R.H. for a total period of 28 days. Curing was called air curing at 45°C and 25% R.H. and was designated as AH.

2. Specimens were covered in plastic sheeting and wet burlap after casting and put in an environmental chamber at 45°C and 25% R.H. After 24 h demoulding took place and specimens were quickly covered with wet burlap and plastic sheeting for further 13 days at the same environmental conditions. Thereafter the covers were removed and specimens were exposed to air at 45°C and 25% R.H. for 14 days (i.e. the total curing period was 28 days). This method of curing was named moist/air curing at 45°C and 25% R.H. and was coded as CH.

3. The specimens were cured in the same way as in (b). The environmental conditions, however, were different. The temperature and relative humidity were respectively 20°C and 55%. Curing was named moist/air

Table 4
Details of the curing methods

Curing	After casting and before demoulding	After demoulding		
	Up to 24 h	After 24 h and up to 14 days	After 14 days and up to 28 days	After 28 days and up to 6 months
AH	Exposed to air at 45°C and 25% R.H.	Exposed to air at 45°C and 25% R.H.	Exposed to air at 45°C and 25% R.H.	N/A
CH	Covered with plastic sheeting and wet burlap at 45°C and 25% R.H.	Covered with plastic sheeting and wet burlap at 45°C and 25% R.H.	Exposed to air at 45°C and 25% R.H.	N/A
CN1	Covered with plastic sheeting and wet burlap at 20°C and 55% R.H.	Covered with plastic sheeting and wet burlap at 20°C and 55% R.H.	Exposed to air at 20°C and 55% R.H.	N/A
CN2	Covered with plastic sheeting and wet burlap at 20°C and 55% R.H.	Covered with plastic sheeting and wet burlap at 20°C and 55% R.H.	Exposed to air at 20°C and 55% R.H.	Exposed to air at 20°C and 55% R.H.
MH	Top surface sprayed with curing membrane at 45°C and 25% R.H.	The other five surfaces were sprayed with curing membrane at 45°C and 25% R.H.	Exposed to air at 45°C and 25% R.H.	N/A

curing at 20°C and 55% R.H. and was designated as CN1.

4. Specimens were cured in the same way as in (c) up to a curing period of 28 days. The specimens continued to be cured in air at 20°C and 55% R.H. for a total curing period of six months. Curing was coded as CN2.

5. After casting specimens were put in the environmental chamber at 45°C and 25% R.H. Before water at the top surface (trowelled face) of the cube had evaporated, the top surface was sprayed with a curing compound. After 24 h specimens were demoulded and the other five faces of the cube were sprayed with curing membrane at the same temperature and relative humidity (i.e., 45°C and 25%). Specimens continued to be cured for further 27 days. Curing was called membrane curing at 45°C and 25% R.H. and was called as MH.

2.3. Drying

After the predetermined curing period of 28 days from casting (except specimens subjected to CN2 curing where the total of curing period was six months), specimens for porosity and pore size distribution measurements were taken from the side surface of the cubes (samples were not taken from either the top surface or the bottom surface of the cube). The mass of each sample ranged from 0.8 to 2.5 g. Samples were dried in an oven at 100 ± 5°C until constant mass. Prior to oven drying, samples were introduced to a hot environmental chamber at 45°C and 25% R.H. The samples were then transferred to an air-tight container until the time of the mercury intrusion porosimetry test.

2.4. Mercury intrusion porosimetry

The porosity and pore size distribution were determined using mercury intrusion porosimetry technique. The instrument has a pressure capacity of 200 MPa. The data were computed by using the Washburn equation as follows

$$D = -(4\delta \cos \theta)/P,$$

where D is the pore diameter, P the applied pressure, δ the surface tension which was taken as 484 dynes/cm and θ is the contact angle which was taken as 142°.

3. Result and discussion

The effect of addition of SP on intruded pore volume for paste subjected to different curing regimes is shown in Fig. 1. Although the water to cement ratio is 0.45 in this investigation, which is considered to be high for paste, the intruded pore volume for the paste containing SP is consistently lower than the paste without SP. This seems to be the case regardless of the curing regime adopted and the age of curing. The drop in intruded pore volume due to the addition of SP can vary between 8.5% and 26% depending upon the curing condition. The intruded pore volume of the paste increases under dry curing (AH) compared with pastes which were subjected to some initial moist curing (CN1 and CH). The membrane cured specimens (MH) yielded higher intruded pore volumes than initially moist cured pastes and lower volume than air cured specimens (AH). The intruded pore volume decreases with the age of curing as

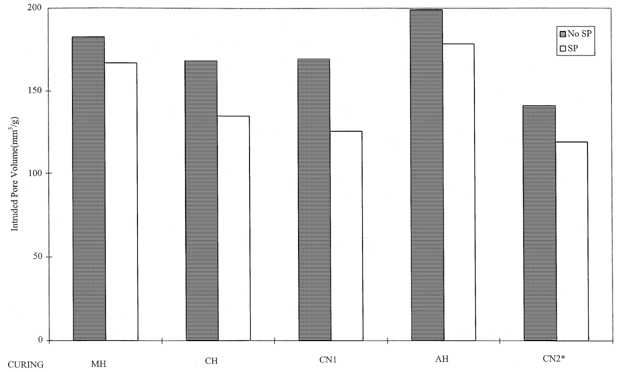

Fig. 1. Influence of superplasticizer on intruded pore volume of paste.

demonstrated by pastes initially subjected to moist curing at 20°C for 14 days (CN1 and CN2) and cured for a total periods of 28 days and six months.

The incremental pore volume versus the mean pore diameter for paste subjected to the different exposure conditions is presented in Figs. 2–6. An observation which can be drawn from these figures is that the dominant pore diameter did not significantly change with the addition of SP. The dominant pore size is the diameter whose size occupies the largest proportion of pores compared with other pore diameters (sizes). The dominant pore size shifts to a smaller value for pastes subjected to some initial moist curing compared with paste exposed to dry curing. The data from these figures were used to determine the threshold diameter which is shown in Fig. 7. The threshold diameter is the diameter on the cumulative pore volume curve before which the intruded pore volume rises sharply. Further details about the determination of threshold diameter are given elsewhere [17]. The addition of SP decreases the threshold diameter at all the exposure conditions, indicating that there is a refinement in the pore structure. With regards to the curing regime, initially air cured specimens at high temperature (AH) exhibited a larger threshold diameter than any other curing methods. Initially moist curing specimens at both normal

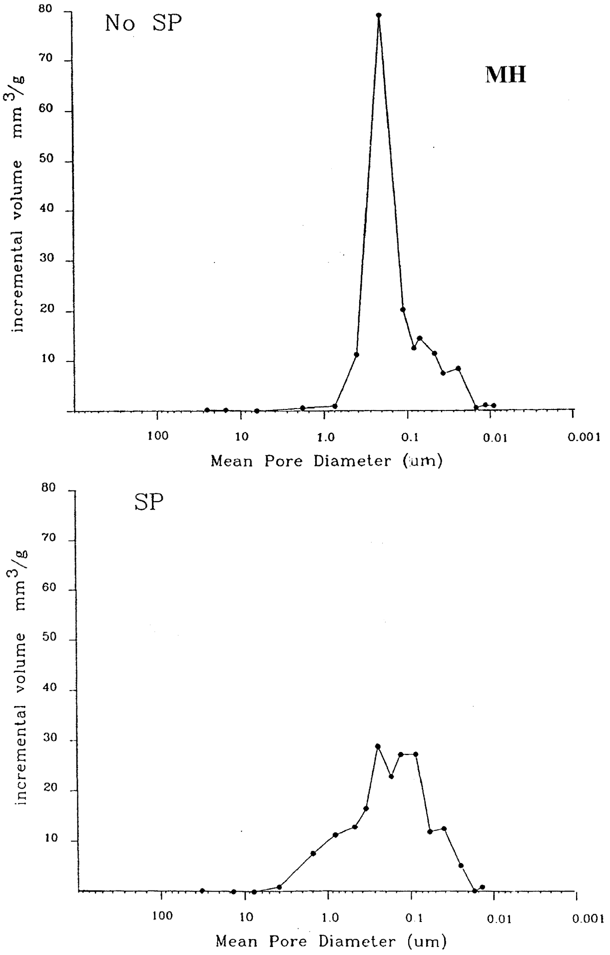

Fig. 2. Influence of superplasticizer on pore structure for membrane cured specimens 45°C and 25% R.H. (MH).

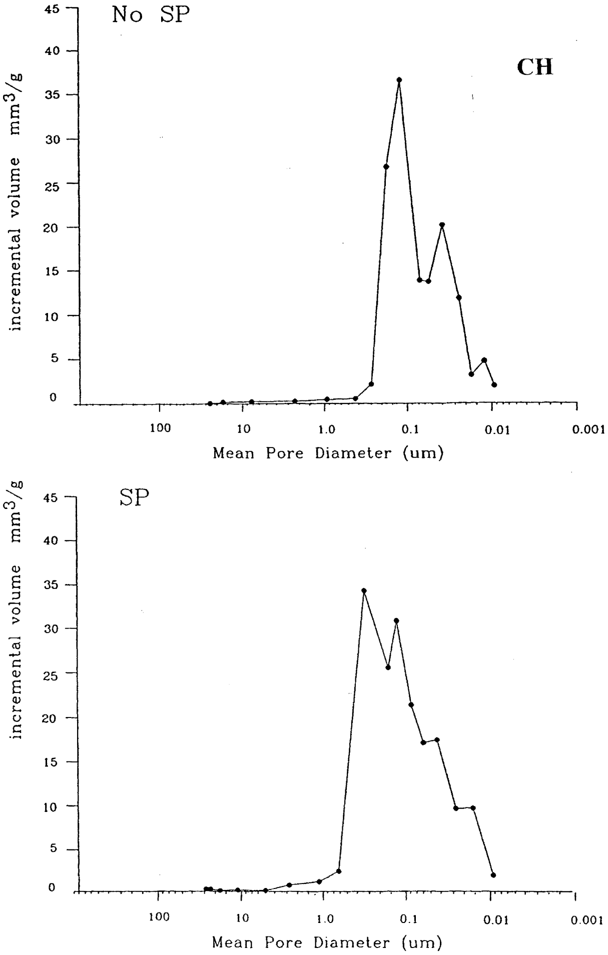

Fig. 3. Influence of superplasticizer on pore structure for moist/air cured specimens 45°C and 25% R.H. (CH).

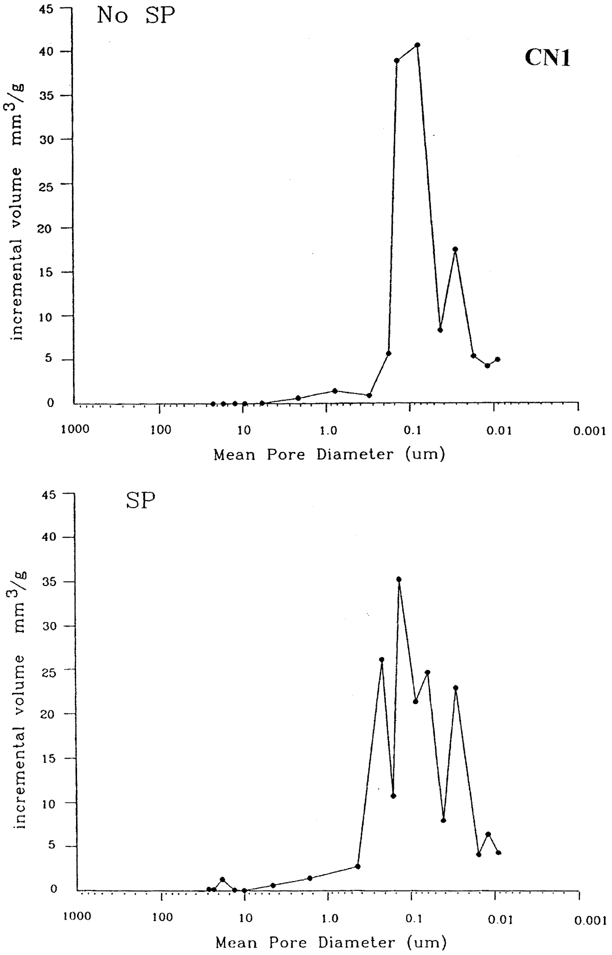

Fig. 4. Influence of superplasticizer on pore structure for moist/air cured specimens 20°C and 55% R.H. (CNI).

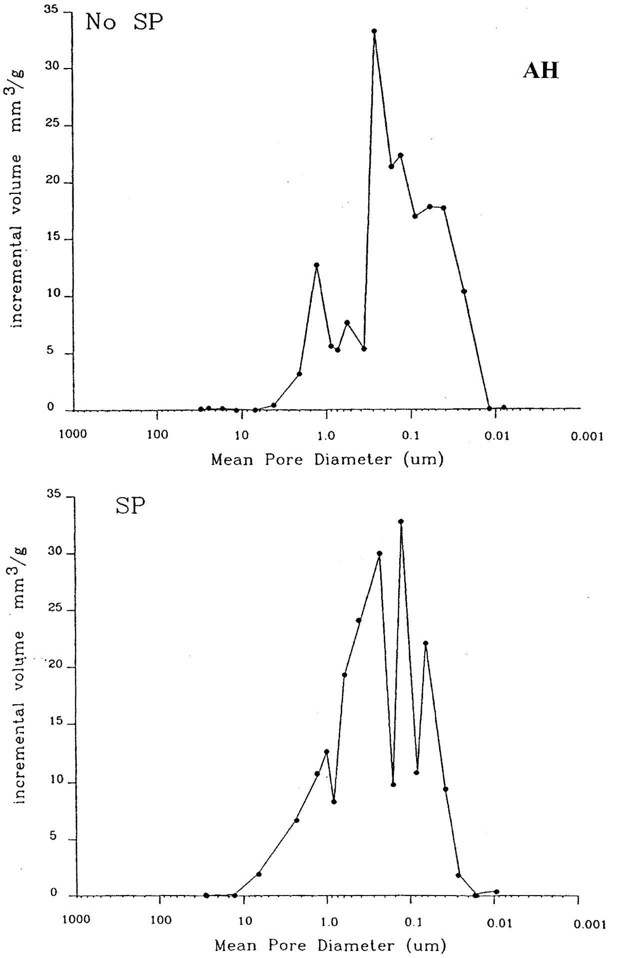

Fig. 5. Influence of superplasticizer on pore structure for air cured specimens 45°C and 25% R.H. (AH).

temperature (20°C) and high temperature (45°C) yielded a lower threshold diameters compared with other curing regimes. For pastes which were initially cured at 20°C (CN1 and CN2), the threshold diameter decreases with the age of curing as expected.

It was suggested that the pores in a cement paste may divided into small pores which have a diameter smaller than 100 nm and large pores which have a diameter larger than 100 nm [18]. Based on this assumption the pores of the paste under the various curing conditions were divided into small and large pores, which are presented in Table 5. It is quite noticeable that there is a reduction in large pores due to the presence of SP. This reduction in large pores is present under the various curing regimes adopted and at different periods of curing. The magnitude of this reduction varies between 2% and 10%. As a consequence of reduction in large pores, the volume of small pores is increased. This further indicates that pore structure is finer due to the inclusion of SP. The refinement of the pore structure due to the presence of SP agrees with results reported elsewhere [3,5,9]. The proportion of large pores for paste subjected to dry curing (AH) is substantially higher than that of paste exposed to initially moist curing. An increase of up to 25% in coarse pores can be observed for initially air cured paste at 45°C compared with initially moist cured specimens at the same temperature. The availability of more water in the moist cured pastes produces more hydration products (i.e. C–S–H gel), which has a pore filling effect, resulting in a denser matrix, reduction in pore volume and finer pore structure. Contrary, in dry cured pastes, less water is available for the formation of hydration products, thereby larger pore volume and coarser pore structure are obtained.

4. Conclusion

The following conclusions are based on the work of this study:

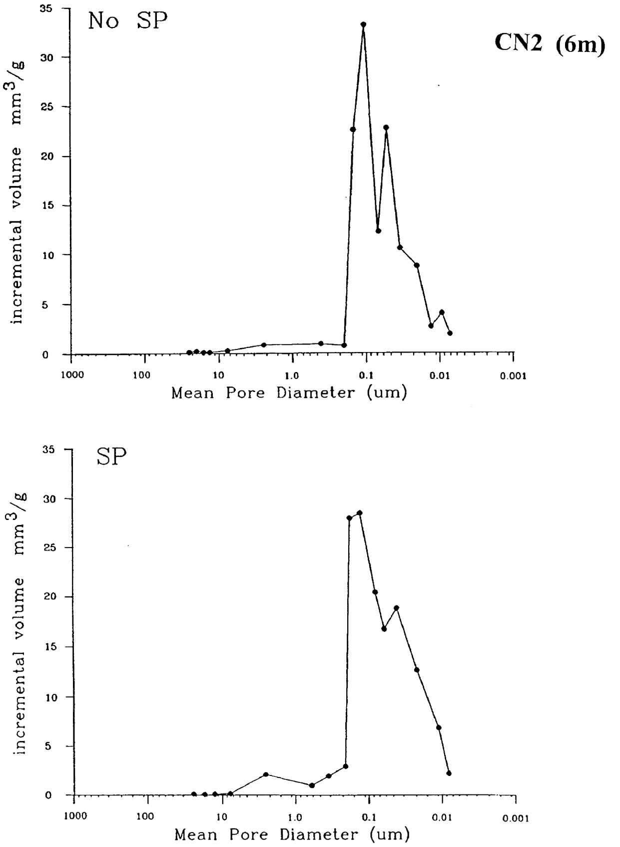

Fig. 6. Influence of superplasticizer on pore structure for moist/air cured specimens 20°C and 55% R.H. (CN2).

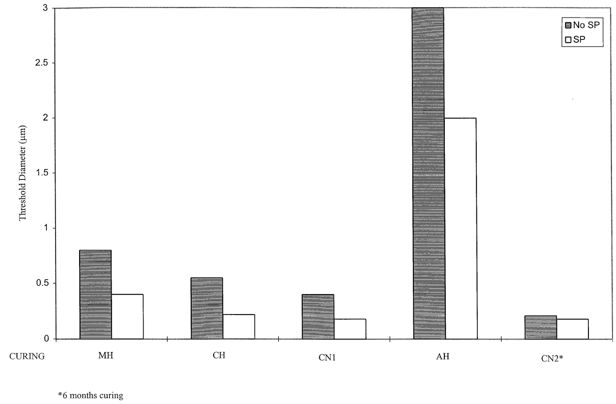

Fig. 7. Influence of superplasticizer on threshold diameter of paste.

The inclusion of SP in cement paste leads to a reduction in the total pore volume and to a refinement of the pore structures. The dominant pore size is unaffected and the threshold diameter is reduced in the presence of SP. The initial curing regime to which a paste specimen is has a substantial influence on porosity and pore structure. Less pore volume and finer pore structure are obtained when cement paste is subjected to initial moist curing as compared with initially dry curing.

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Table 5
Influence of superplasticizer on large and small pores

Curing	Age of curing[a]	SP % bwc (%)	Pore volume (mm^3/g)			% Pores	
			Total volume	Large pores (>100 nm)	Small pores (<100 nm)	Large	Small
MH	28 days	0	182.6	125.4	57.2	68.7	31.3
MH	28 days	1.2	167.0	111.2	55.9	66.5	33.5
CH	28 days	0	168.4	81.8	86.1	48.6	51.4
CH	28 days	1.2	135.2	52.3	82.9	38.7	61.3
CN1	28 days	0	169.5	78.6	90.9	46.4	53.6
CN1	28 days	1.2	125.9	46.5	79.4	36.9	63.1
AH	28 days	0	199.1	138.9	60.1	69.8	30.2
AH	28 days	1.2	178.5	116.8	61.7	65.5	34.5
CN2	6 months	0	141.4	64.1	77.3	45.34	54.7
CN2	6 months	1.2	119.6	45.6	73.9	38.2	61.8

[a] By weight of cement.

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