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Cement and Concrete Research 34 (2004) 1043–1049

CEMENT AND CONCRETE RESEARCH

Properties of high-volume fly ash concrete incorporating nano-SiO_2

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Received 22 August 2002; accepted 20 November 2003

Abstract

This paper presents a laboratory study on the properties of high-volume fly ash high-strength concrete incorporating nano-SiO_2 (SHFAC). The results were compared with those of control Portland cement concrete (PCC) and of high-volume fly ash high-strength concrete (HFAC). Assessments of these concrete mixes were based on short- and long-term performance. These included compressive strength and pore size distribution. Significant strength increases of SHFAC compared to the high-volume fly ash high-strength were observed as early as after 3 days curing, and improvements in the pore size distribution of SHFAC were also observed. In this work, the hydration heat of nano-SiO_2 fly ash cement systems was also studied in comparison to the fly ash–cement systems and to the pure cement systems. In addition, the weight change of fly ash incorporating nano-SiO_2, fly ash, and nano-SiO_2 alone after immersed in saturated lime solution was also studied.

Keywords: Nano-SiO_2; High-performance concrete; Compressive strength; Pore size distribution

1. Introduction

Fly ash is a by-product of coal-fired electric power stations. It improves the durability when used in concrete as a cement replacement. It also contributes to concrete strength by pozzolanic and filler effects. Recently, fly ash has been increasingly used in the concrete industry. In some cases, large volume of (>40%) fly ash is used to achieve desired concrete properties and lower the cost of concrete production [1,2]. However, as pozzolanic reaction is a slow process that its contribution to strength occurs only at later ages, the early strength of concrete will be significantly reduced if a large amount of fly ash is used [3,4]. This limits the wide use of high-volume fly ash concrete by engineers. Different approaches are used to accelerate the pozzolanic reaction of fly ash and therefore increase the early strength of the concrete containing fly ash. These approaches include (i) mechanical treatment (grinding), (ii) accelerated curing and autoclaving, and (iii) chemical activating [5–8]. Chemical activating involved using alkali activation and sulfate activation [9–11]. However, alkali activation used in concrete may lead to alkali–silica reaction [12], and sulfate activation may decrease the durability of concrete due to the large ettringite contents.

Studies have shown that the hydration heat indicates the activation of pozzolanic materials [13]; if the materials show high pozzolanic activity, the heat produced during hydration is higher. This fact becomes more evident in materials with high pozzolanic activity as the case of silica fume, which produces an increase in heat evolution of hydrating cement, compared to Portland cement (PC). However, materials with low initial activity, such as fly ash, decrease the hydration heat.

Nano-SiO_2 has been added to polymer to increase strength, flexibility, and aging resistance [14,15]. In this paper, an effort was made to investigate the effect of nano-SiO_2 in improving the properties of high-volume fly ash high-strength concrete (HFAC). The hydration heat, the strength development, and the pore size distribution of concrete were investigated. A comparison was also made among fly ash incorporating nano-SiO_2, fly ash, and nano-SiO_2 alone in terms of weight change after immersed in saturated lime solution.

2. Experimental program

2.1. Materials

The cementitious materials used in this test were PC, fly ash. Their chemical compositions and physical prop-

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0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.11.013

erties are given in Table 1. Nano-SiO_2 used in this paper was purchased from Zhoushan Mingri Nanometer Material, its physical properties are given in Table 2, X-ray diffraction (XRD) pattern (Fig. 1) indicated that the crystallinity of nano-SiO_2 was low. The crystallinity of fly ash also was low, the main crystalline components of fly ash were quartz and mullite. Coarse aggregate was crushed rock with a maximum size of 20 mm and a specific gravity of 2.70. The fine aggregate was natural sand with a fineness modulus of 2.35 and a specific gravity of 2.50. Details of the mix proportions for concretes are given in Table 3. The control mix was cast using PC, while the other mixes were prepared by replacing part of the cement with different mineral admixtures on mass-for-mass basis. The same water/binder ratio of 0.28 was used for the concrete mixes with different amount of superplasticizer so that the fluidity of concretes did not change due to the effect of the different mineral admixtures. The superplasticizer used in this paper is a primrose power, its properties is up to the GB8076-1997 (China standard). The superplasticizer contains 90% calcium salt of a condensed naphthalene sulfonic acid, contains less than 0.06% Cl^-, and contains 5–10% R_2O.

2.2. Test procedure

In order to well-disperse nano-SiO_2 into concrete, cement, fly ash, nano-SiO_2, and acetone were milled together for 40 min in a blender. Then the mixture was dried in a vacuum oven. To contrast, cement and fly ash mixture was also milled 40 min in blender. All concrete mixtures were mixed in a pan mixer, following the procedures recommended by Chinese Standard JGJ 55-96. After mixing, a vibrating table was used to ensure good compaction. The surface of the concrete was then smoothed, and wet cloth was used to cover the concrete until the specimens were demolded 1 day after casting.

Table 1
Chemical and physical properties of cement and FA (%)

	Cement	FA
Specific gravity	3.05	2.45
Compressive strength, 28 days (MPa)	56.7	–
Pozzolanic activity index, 28 days (%)	–	86.5
Specific surface, Blaine (m^2/kg)	392	521
SiO_2	20.6	61.7
Al_2O_3	4.0	21.3
Fe_2O_3	3.1	7
CaO	62.8	4.5
MgO	2.6	1.99
SO_3	3.1	0.35
Na_2O	–	0.48
K_2O	–	0.5
LOI	1.8	1.9

Table 2
The physical properties of nano-SiO_2

Type	BET-specific area (m^2/g)	Average particle size (nm)	Ultraviolet reflection rate (%)	SiO_2 content (%)	Apparent density (g/cm^3)
SP1	640 ± 50	10 ± 5	85	≥ 99.9	$\leqq 0.15$

Compressive strength tests were carried out on 150-mm cube specimens, according to Chinese Standard GB-8185. In the experiment, the specimens were cured in water at room temperature. The specimens were dried 24 h prior to testing for every mix at the required age, and the average strength of three specimens was used as an index.

The tests of pore structure of the concrete samples were conducted by using a mercury intrusion porosimeter. The maximum pressure of the porosimeter was 210 MPa. Values of 140° and 485.0 dyn/cm were used for the contact angle and mercury surface tension. The samples were dried in an oven at 50 °C for 24 h before test.

The hydration heat tests were carried out using a thermally isolated bottle, the test was carried out in a constant temperature room at 20 ± 2 °C. The heating (°C) is used to calculate the hydration heat developed by the test sample.

In this paper, a new test method was used to evaluate the degree of hydration; the method was based on the following chemic equation of cementitious materials:

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO.2SiO_2.H_2O$$

$$Al_2O_3 + 3Ca(OH)_2 + 3H_2O \rightarrow 3CaO.Al_2O_3.6H_2O$$

The weight change over time of cementitious materials can evaluate their pozzolanic activity. In this work, the weight change over time of fly ash incorporating nano-SiO_2, fly ash, and nano-SiO_2 alone after immersed in saturated lime solution was tested. The containers used in this paper are vitreous desiccators (Fig. 2) full of saturated lime. These desiccators were kept in a constant temperature room (40 ± 2 °C). The cementitious materials were put in

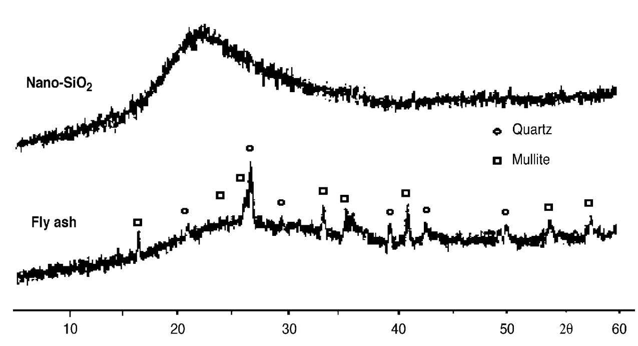

Fig. 1. XRD of fly ash and nano-SiO_2.

Table 3
Mix proportions of concretes (kg/m^3)

Binder combination	Binder				Water	Aggregate		W/B[a]	Superplasticizer[b] dosage
	PC	FA	Nano-SiO_2	Total		Fine	Coarse		
PCC	500	–	–	500	140	659	1162	0.28	1.7
HFAC	250	250	–	500	140	644	1135	0.28	1.5
SHFAC	230	250	20	500	140	647	1140	0.28	2.0

[a] Water/binder (i.e., PC plus additional materials) ratio.
[b] Dosages given as percent of total binder content by mass.

vitreous cups, which were covered by a qualitative filter paper (ion can go in and out freely, and fly ash particle or nano-SiO_2 cannot leak); to prevent filter paper from broken, a piece of gauze was covered. These vitreous cups were immersed in saturated lime solution at for 3 h, 12 h, 1 day, 7 days, and 28 days. At the end of each period, each mix was leached by using a filter paper, soaked in pure alcohol for 7 days to stop further hydration, and then dried in an oven at 50 °C to absolute desiccation before test. The rate of weight change was obtained by contrasting the increment weight of each mix after immersed in saturated lime solution to the original weight at the end of a given period.

3. Experimental results and discussion

3.1. Hydration heat

Fig. 3 shows the evolution of heating for the different concrete. Results obtained show how the maximum heating occurs and depends on the type of addition. High-volume fly ash concrete delays this maximum heating, which occurs at around 30–40 h. The maximum heating of SHFAC is similar to that of Portland cement concrete (PCC), which occurs at around 15–25 h. These results also show that the maximum temperature depends on the type of addition. The maximum temperature reached for PCC is about 65 °C, that of SHFAC is slightly lower than that of PCC about 61 °C, and the maximum temperature of HFAC is the lowest, which is about 51 °C.

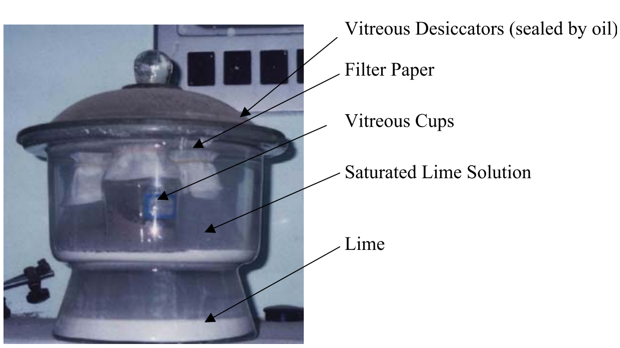

Fig. 2. Test method of weight change of cementitious materials.

These results indicate that there are two different effects to be considered regarding the behavior of materials: on one hand, the PC hydration heat; on the other hand, the influence of substituting PC by additions, which may simply dilute the effects of PC hydration or may accelerate PC hydration. In the case of HFAC, due to fly ash has low initial activity and the weight of PC in HFAC is only half of that in PCC, the temperatures of HFAC rise slower and the maximum temperature is lower. In the case of SHFAC, temperatures rise faster and the maximum temperature is higher than that of HFAC; this is because that nano-SiO_2 has high activity and large specific surface (64,000 m^2/kg) and can provide a large number of nucleating site, which means that nano-SiO_2 can activate fly ash as well as cement.

3.2. Weight change over time

The results obtained for pozzolanic activity are shown in Fig. 4. Weight increment (ΔW) is subtracted the original weight from the total weight (which was the actual test value); for example, the total weight of 100 g fly ash after immersed in saturated lime solution for 168 h is 118 g and weight increment (ΔW) of fly ash is 18 g. From Fig. 4, we can see that (after 1 h) both nano-SiO_2 and FA incorporating nano-SiO_2 show strong pozzolanic activity since the weight of samples increased; while the FA, due to its lesser activity at early stages, hardly shows any reaction with lime before 168 h. It also can be seen from Fig. 4 that the weight increment (G_{SFA}) of 100 g FA incorporating 4 g nano-SiO_2 is larger than the weight increment of FA (G_{SFA}) plus the weight increment of nano-SiO_2 (G_S) ($G_{SFA} > G_{FA} + G_S$) at each tested age. This result indicates that nano-SiO_2 can activate fly ash when existing lime.

The rate of weight change [weight increment (ΔW)/original weight] of each mix is shown in Fig. 5. For nano-SiO_2, during the first 24 h of the test, reaction is extraordinary rapid, which makes the ascending slope of the curves very steep. Though the rate of weight change of 100 g FA incorporating 4 g nano-SiO_2 is slower than that of 4 g nano-SiO_2, it is faster than that of 100 g fly ash.

3.3. Development of compressive strength

Fig. 6 shows the strength development of PCC, HFAC (containing 50% FA), and the concrete (SHFAC) incor-

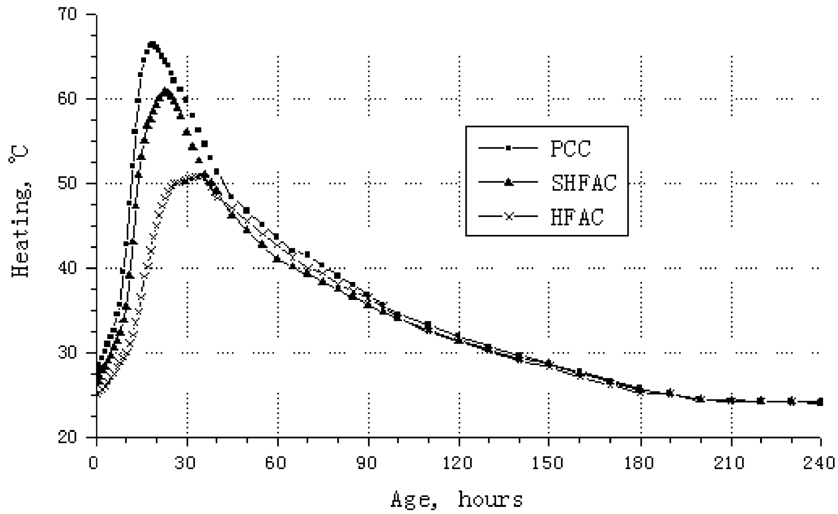

Fig. 3. Heating over time.

porating a combination of 50% FA and 4% nano-SiO_2. From this figure, we can see the general trend of increasing strength with age up to 2 years for all concretes. As expected, the behavior of HFAC at early ages is different from that of PCC and SHFAC. Though it has high strength at the end test age, its strength development is the slowest before 1 year. The strength development of SHFAC is similar to that of PCC, only with slightly lower values before 56 days. Compared with the results of HFAC, the early age compressive strength of high-volume fly ash was significantly increased when 4% nano-SiO_2 was added. Fig. 6 shows that the addition of 4% nano-SiO_2 increased the 3-day compressive strength by about 81%. It also increased the strength at the later ages. This indicates that SHFAC can achieve adequate early compressive strength while maintaining a high long-term strength.

Table 4 shows the strength gain of the concretes between 28 days and 2 years. PCC obtains a strength increase of 27.9% during this period. The compressive strength of SHFAC increases 52.9%, higher than that of PCC, but lower than that of HFAC (99.4%).

3.4. Pore size distribution

The pore size distribution of concrete was shown in Figs. 7 and 8. From Fig. 7, we can see that fly ash replacements in concrete increased both the pore size and the total porosity. When high-volume fly ash cement systems incorporating nano-SiO_2, the cumulative mercury intrusion curve for concrete lies on the finer side, and there is little difference between SHFAC and PCC existing in the pores with diameter larger than 0.05 um. This is because fly ash is a lesser activity pozzolanic material. After short time curing, there is a

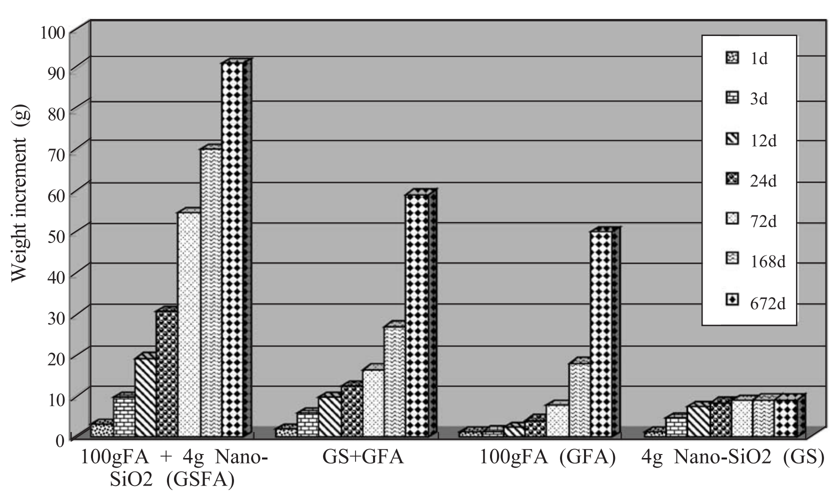

Fig. 4. Weight change in saturated lime solution.

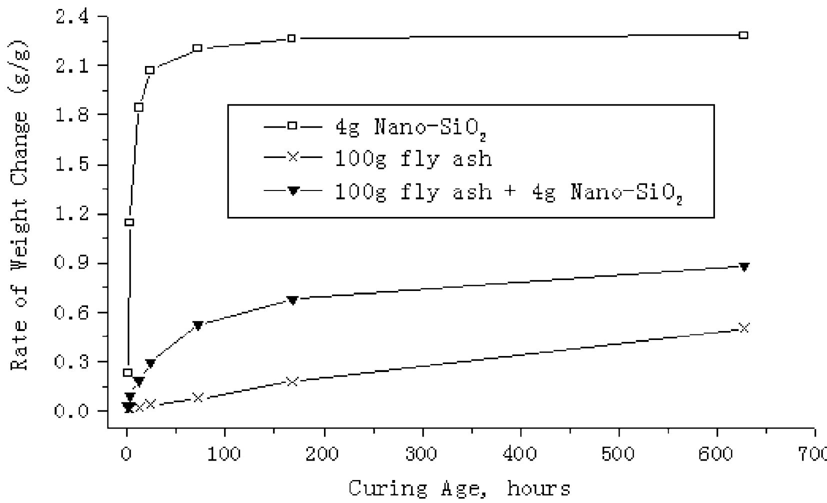

Fig. 5. Rate of weight change, weight increment compared to the original weight.

number of unhydrated fly ash in high-volume fly ash cement system, and the addition of fly ash in concrete leads to higher porosity and larger pore size. However, when nano-SiO_2 was incorporated due to its high activity and nucleating site effects, the pore size of concrete refines and the porosity lowers even at short time curing.

The pore size distribution of concrete at the age of 2 years was shown in Fig. 8. It can be seen that as the curing age increased, the pore sizes (from 0.005 to 1000 um) of all the samples become significantly smaller. The major difference between HFAC and PCC existed in the pores with a diameter larger than 0.03 um; fly ash used in this study is effective in the refinement of the pore structure of the concrete. The cumulative mercury intrusion curve for SHFAC lies on the finest side.

4. Conclusions

The results and conclusions are summarized as follows:

1. Fly ash has low initial activity, but the pozzolanic activity significantly increased after incorporating a little nano-SiO_2. This has been confirmed by the tests carried out on pozzolanic activity (weight change in lime solution) and hydration heat.
2. According to the heating definition, concrete with 50% FA incorporating 4% nano-SiO_2 can reach "higher" about 61 °C, which slightly lowers than that of PCC about 65 °C and higher than that of HFAC about 51 °C. It means an increase in temperature of 19% with respect to HFAC.

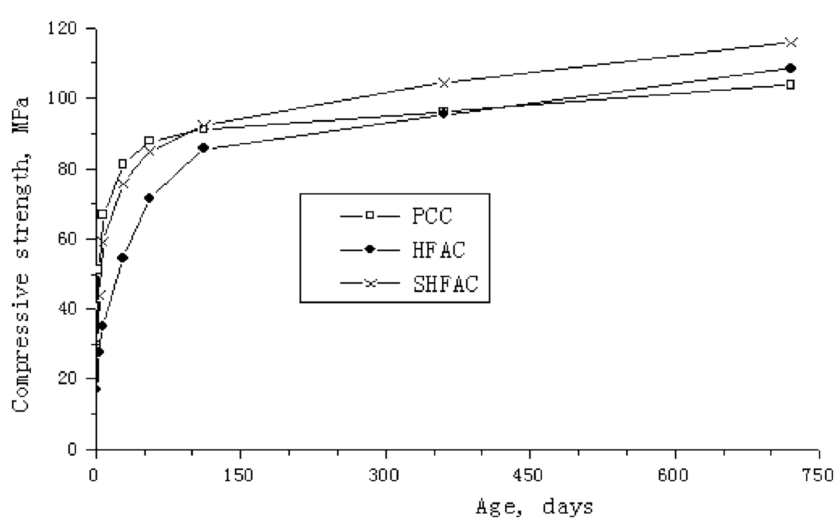

Fig. 6. Development of the compressive strength versus time.

Table 4
Compressive strength gain of concretes

Binder combination	Cube compressive strength (MPa)								Strength gain from 28 days to 2 years (%)
	1 days	3 days	7 days	28 days	56 days	112 days	360 days	720 days	
PCC	40.5	51.2	66.8	81.1	87.9	91.2	96.3	103.7	27.9
HFAC	16.8	27.6	35.0	54.4	71.6	85.7	95.4	108.5	99.4
SHFAC	30.4	43.9	59.0	75.8	85	92.2	104.5	115.9	52.9

3. The pozzolanic activity results (weight change) showed that nano-SiO_2 can activate fly ash, and the weight increment of fly ash incorporating nano-SiO_2 (G_{SFA}) at each tested age was higher than that of fly ash plus that of nano-SiO_2 ($G_S + G_{FA}$).
4. Addition of nano-SiO_2 to high-volume high-strength concrete leads to an increase of both short-term strength and long-term strength. SHFAC has an increase in 3-day strength of 81% with respect to HFAC, and the 2-year strength was 115.9 MPa higher

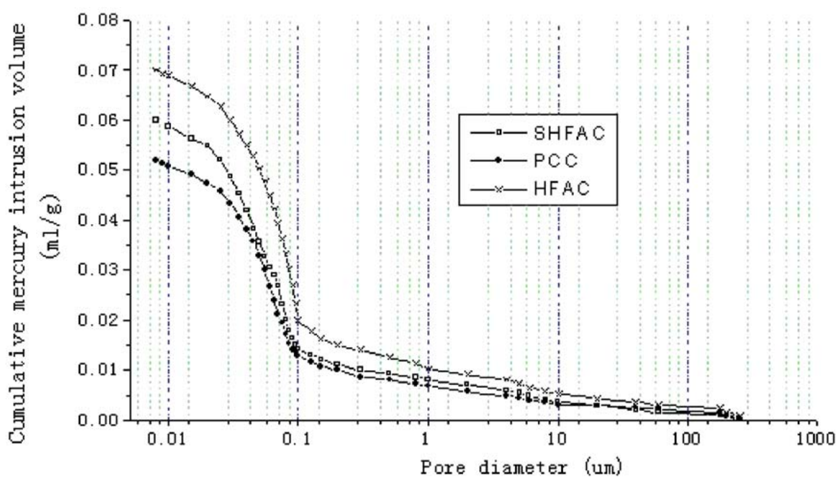

Fig. 7. Porosity measurements at 28 days for different concretes.

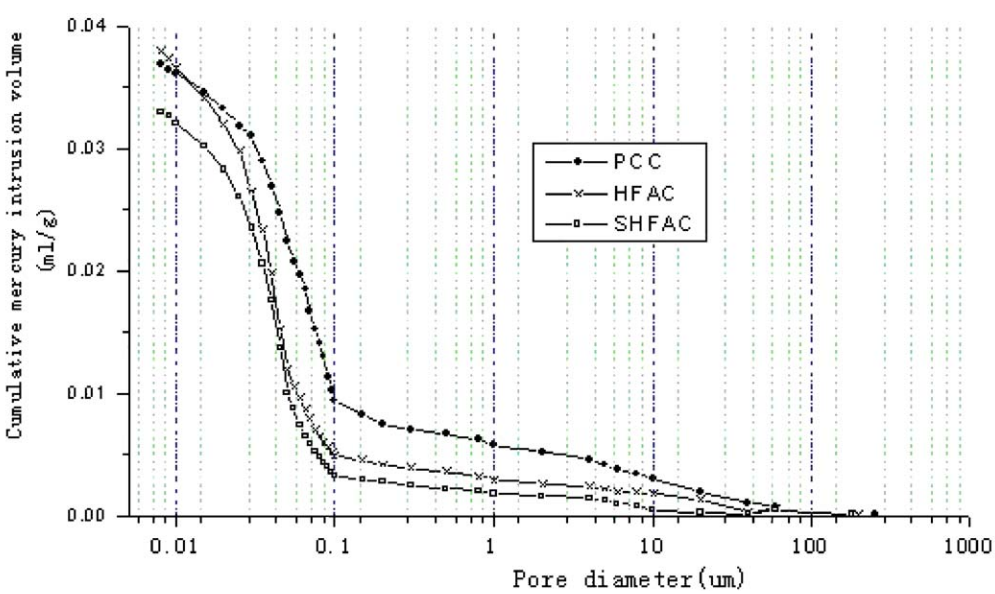

Fig. 8. Porosity measurements at 2 years for different concretes.

than both of HFAC about 108 MPa and of PCC about 103.7 MPa.

5. The addition of fly ash leads to higher porosity at short curing time, while nano-SiO_2, acting as an accelerating additive, leads to more compact structures, even at short curing times.

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