

The effects of type of cement and curing methods on the pore structure of concrete

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Abstract

The resistance of cementitious materials to chemical attack or physical degradation is related to the mechanical properties of the material, but more importantly the chemical and microstructural characteristics and particularly the pore structure of the hardened material. Given information about pore structure, Mercury Intrusion Porosimetry (MIP) is a technique that can provide such information which has improved significantly in pressuring capacity and in operational convenience. By measuring the amount of mercury intruded into the pores of a solid sample, the porosimeters give valuable data from which cumulative volume and pore size distribution, porosity as well as pore surface area can be determined. In this work, five concrete mixtures are prepared with water/cementitious material ratio 0.4 to investigate the effect of using different types of supplementary cementing materials and curing methods on the pore structure of concrete. The measured properties of fresh concrete include slump, air content and unit weight while the measured properties of hardened concrete include compressive strength, flexural strength, tensile strength, pulse velocity and dynamic young's modulus as well as the pore structure characteristics which involve, porosity, cumulative intrusion volume, pore surface area, and pore size distribution. These properties are measured according to the specifications provided by Japanese Industrial Standard (JIS) after 28 days of curing.

1 Introduction

The durability of concrete in service depends very much on the micro-porosity of its outer surface zone. Only a good quality concrete cover zone can impede the rapid ingress of deleterious species such as; water, chlorides and carbon dioxide and therefore delay the onset of corrosion of steel reinforcement. The use of pozzolanic materials and reduced water/cementitious material ratio to produce

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high performance concrete are quite common [1]. The pore structure of a porous solid is usually described by the volume of pores per unit volume of the material (i.e., porosity) and by the size and spatial distribution as well as the interconnectivity of these pores. Pore structure influences the physical properties (such as strength, toughness, elastic properties, permeability and the effective diffusivity) and the environmental stability (such as the durability and reliability) of engineering materials, and is an important means of controlling the life expectancy and the economics of use of a material or structure [2].

The open pore volume distribution, when plotted against the logarithm of the pore diameter, is generally found to follow a normal distribution. Many materials have more than one size distribution of pores. For example, cement pastes contain two interpenetrating pore systems, with capillary pores originating primarily from the mixing water, and gel pores that represent the inherent structure and porosity of cement hydration products [3].

The most important characteristics of pore system are porosity and pore size distribution, which can be determined through mercury intrusion porosimetry. The smallest size of pore, in which mercury can intrude, depends upon the maximum intrusion pressure applied. Consequently, extent of porosity that can be determined by porosimetry test depends upon the nature of the pores, the size of the smallest pore likely to be encountered in the material and the maximum intrusion pressure applied. The pore system in cement paste materials consists of four types of pores. There are: (a) gel pores, which are micropores of characteristic dimension 0.5-10 nm; (b) capillary pores, which are mesopores with average radius ranging from 5 to 5000 nm; (c) macropores due to deliberately entrained air; and (d) macropores due to inadequate compaction. In concrete, in addition to the above pores, there can be cracks at aggregate-mortar interface due to shrinkage [4].

The studies of Parrott [5] suggest that the porous gel in hydrated cement will shrink, even with quite moderate drying. The shrinkage of the gel seems to derive from a reduction in volume of the small pores, without any change in total porosity. Thus the volume of large pores is increased and the rate of diffusion is correspondingly increased. Therefore, the pore structure of concrete, perhaps more than any other characteristic of the materials, affects the behavior of the concrete [6]. This influence is such important that the strength, durability, and permeability of certain materials can be estimated.

2 Experimental program

Five types of concrete were prepared to investigate the effect of cement type and curing method on the pore structure characteristics of concrete. The values of water/cementitious material and sand/aggregate ratios were 0.4 and 0.5, respectively. The studied parameters represent properties of fresh concrete including slump, air content, and unit weight, while, properties of hardened concrete including compressive strength, tensile strength, flexural strength, dynamic Young's modulus and pulse velocity. Furthermore, the pore structure characteristics of concrete involve, porosity, cumulative intrusion volume, pore surface area, and pore size distributions are investigated.

The materials that are involved in the experimental work selected from local sources in Japan. The used cementitious materials were, Ordinary Portland Cement (OPC), Blast-Furnace Slag Cement (BFSC), Ordinary Portland Cement with Silica Fume (SFC), Fly Ash Cement (FAC), and Sulfate Resisting Cement (SRC). The properties of the used cementitious materials comply with Japanese Industrial Standard. The used silica fume (SF) powder has specific surface area of $20 \text{ m}^2/\text{gm}$, average diameter of $0.15 \mu\text{m}$, silicon dioxide of 97%, and specific gravity of 2.20. The used sand has 2.55 specific gravity, 2.49 of fineness modulus and 1.62 % of the water effective absorption. The coarse aggregate is crushed basalt of 2.61 specific gravity, 15 mm of nominal maximum size, and 6.18 of fineness modulus. The used chemical admixture is superplasticizer, high range water reducing agent, with dose 1.4% by cement weight. The mix proportions details of concrete mixtures are listed in Table 1.

Table 1 : Mix proportions details for the studied concrete.

Cement type	OPC	BFSC	SFC*	FAC	SRC
Cement content, kg/m^3	400				
Water, liter/m^3	160				
Sand, kg/m^3	877	871	870	868	881
Gravel, kg/m^3	898	892	891	888	902
Admixtures, liter/m^3	5.6				

*SFC: 10% Silica Fume (SF) + 90% OPC

The materials batched into the mixer are as follows: first; coarse aggregate followed by sand, then cement added to the mixer. The mixing time is three minutes, starting with 1.5 minutes dry mixing and then the required water (mixed with chemical admixture) is added for the next 1.5 minutes of mixing. After casting, the concrete specimens were compacted by the use of a vibrator. The samples were finished, stripped from their molds the day after casting. The samples were cured for 28 days with two different methods of curing. In the first method of curing (A), specimens were immersed in water till the testing time while in the second method of curing (B) specimens maintained at 22°C and 80 % relative humidity and sprinkled with water two times a day for seven days.

Concrete specimens (cylinder of 10 cm diameter and height 20 cm) were firstly used to measure the non-destructive parameters (pulse velocity and dynamic modulus of elasticity). Secondly, the compression test was performed. The mercury porosimetry description, sample preparation and testing procedures are described in details in ref. [7].

3 Properties of fresh and hardened concrete

The obtained test results show that the incorporation of cementitious materials (minerals admixtures) in concrete (whether in the form of additions to cement like blast furnace slag and fly ash or as admixtures to concrete like silica fume) lead to a general enhancement in measured properties of freshly concrete. Also,

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results show that the type of cement plays significant role in produced fresh concrete properties as represented in Table 2. The concrete slump values range from 19.2 cm to 22.2 cm except for the mix of SFC which shows 8.5 cm due to large specific surface area of SF. Moreover, air content is one of effected properties of the produced fresh concrete due to change in the type of cement. Air content values range from 1.5% to 3.1% and SFC mix shows the highest air content while SRC mix shows the lowest ones. Furthermore, the unit weight of concrete changes according to the type of used cement, this is due to the change in the specific gravity of cements.

Table 2: Properties of fresh concrete.

Cement type	OPC	BFSC	SFC	FAC	SRC
Slump (cm)	19.2	21.6	8.5	22.2	20.2
Air content (%)	1.80	2.50	3.10	2.30	1.50
Unit weight (t/m ³)	2.384	2.353	2.312	2.322	2.388

Table 3: Properties of hardened concrete after 28 days of curing.

Concrete property	Curing type	Cement type				
		OPC	BFSC	SFC	FAC	SRC
Compressive strength (kg/cm ²)	A	464	452	611	479	583
	B	475	404	555	452	506
Tensile strength (kg/cm ²)	A	41.1	36.0	38.7	39.4	51.1
	B	35.2	30.8	36.9	34.9	35.8
Flexural strength (kg/cm ²)	A	86.0	68.4	87.8	73.6	79.2
	B	75.5	64.3	82.2	64.5	69.8
Pulse velocity (km/sec)	A	4.70	4.67	4.70	4.63	4.82
	B	4.60	4.53	4.58	4.52	4.62
Dynamic Young's modulus (x10 ⁵ kg/cm ²)	A	4.29	4.24	4.43	4.27	4.59
	B	4.18	3.79	4.11	4.02	4.31

The compressive strength of concrete has come to be accepted as a very good indicator of its overall quality [8]. The obtained test results of the mechanical properties of hardened concrete after 28 days of curing are listed in Table 3. The compressive strength values are higher than 450 and 400 kg/cm² for all mixtures with curing A and B, respectively. The concrete of SFC shows the highest value of compressive strength while BFSC concrete shows the lowest ones with the two types of curing. Moreover, the measured values for both of tensile strength and flexural strength tests show approximately similar trend to that of the compressive strength. The ratios between results of the two curing methods (B/A) range from 0.87 to 0.91, 0.70 to 0.95 and 0.88 to 0.94 for compressive strength, tensile strength and flexural strength, respectively. The results of concrete of curing A show higher compressive strength, tensile strength, flexural strength than those of curing B.

As for the mechanical properties, the results of the nondestructive tests (pulse velocity and vertical dynamic Young's modulus) for the concrete of curing A are higher than those of curing B. The difference between results of the two curing types about 5% and 10% for the pulse velocity and vertical dynamic Young's modulus, respectively. There is a considerable agreement between the obtained data of compressive strength and both of pulse velocity and dynamic Young's modulus. Also, all the measured properties of concrete are affected due to change in type of cement and concrete containing silica fume is acknowledged to have higher mechanical properties than other studied concrete.

4 Mercury porosimetry theory

Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law, in the case of a non-wetting liquid like mercury and cylindrical pores, is expressed by the Washburn equation :

$$D = 4\gamma \cos \varphi / P \quad (1)$$

where D is pore size diameter, P the applied pressure, γ the surface tension, and φ the contact angle, all in consistent units. The volume of mercury V penetrating the pores is measured directly as a function of applied pressure. This P-V information serves as a unique characterization of pore structure.

Pores are rarely cylindrical, hence the equation 1 constitutes a special model. Such a model may not best represent pores in actual materials, but its use is generally accepted as the practical means for treating what, otherwise, would be a most complex problem. The surface tension of mercury varies with purity; its usually accepted value and the value recommended here is 485 dynes/cm. The contact angle between mercury and the solid containing the pores varies somewhat with solid composition. A value of 130 degrees is recommended in the absence of specific information to the contrary.

Mercury extruding from upon reduction of pressure is in general accord with the equation 1, but indicated pore diameters are always offset toward larger diameters. This results from equivalent volumes of mercury extruding at pressures lower than those at which the pores were intruded. It is also commonly observed that actual pores always trap mercury. The first phenomena is usually attributed to receding contact angles being less than advancing ones. The second is likely due to pore irregularities giving rise to enlarged chambers and "ink-well" structures. These phenomena give rise to hysteresis phenomena, i.e., distinct intrusion and extrusion P-V curves [7]. The poresizer 9320 V2.08 (mercury intrusion porosimetry) have been used here to measure the pore structure characteristics of tested concrete.

5 Pore structure characteristics

Until recently, the knowledge of nature and behavior of concrete was restricted to a few phenomenological properties. In past few decades, concrete technologists have focused their attention on the internal structure of concrete.

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The internal structure of concrete represented by its pore system, i.e., the porosity and pore size distribution, plays a decisive role in influencing the physical and mechanical properties of concrete. The most valued properties such as compressive strength and durability of hardened concrete are directly related to its pore structure [9].

The measured results of pore structure characteristics of tested concrete at 28 days are summarized in Table 4. The results confirm the fact that cumulative intrusion volume is changed by type of curing as well as used cementitious materials type. Where, OPC and BFSC concrete of curing A show higher cumulative intrusion volume than those of Curing B, while the measured values of SFC, FAC and SRC concrete of curing A are lower than those of curing B. Furthermore, FAC indicates highest values of cumulative intrusion volume with both type of curing and SFC and OPC concretes show the lowest values with curing A and B, respectively. The obtained results depend on the hydration of the pozzolanic materials which has a direct effect on pore volume by the increase in gel volume and decrease in pore volume.

Table 4 : Summary of pore structure characteristics at 28 days.

Pore structure characteristics	Curing type	Cement type				
		OPC	BFSC	SFC	FAC	SRC
Cumulative intrusion volume (mL/g)	A	0.0475	0.0506	0.0407	0.0623	0.0515
	B	0.0453	0.0471	0.0457	0.0636	0.0635
Cumulative porosity (%)	A	10.35	10.79	9.33	13.40	11.48
	B	10.17	10.07	10.32	13.68	14.00
Cumulative pore area (sq-m/g)	A	6.914	8.134	5.656	10.136	7.749
	B	5.635	6.486	5.315	7.047	6.728
Maximum pore diameter (μm)	A	147.78	154.69	147.97	147.93	137.66
	B	153.53	147.40	160.39	161.97	147.40
Minimum pore diameter (μm)	A	0.0060	0.0060	0.0060	0.0060	0.0060
	B	0.0060	0.0060	0.0060	0.0060	0.0060
Average pore diameter (μm)	A	0.0275	0.0249	0.0288	0.0246	0.0266
	B	0.0321	0.0290	0.0344	0.0361	0.0377

Roy [10] reported that adding mineral admixture to concrete leads to decrease in pore size or increase in the fraction of porosity in the finer pore. Moreover, the pores are blocked by the effect of hydration products, causing change of pore structure such as the formation of fine and discontinuous pores. The results of the cumulative porosity of tested concrete, listed in Table 4, show approximately the same trend as the measured cumulative intrusion volume. The measured cumulative porosity indicates that concrete of SFC shows the lowest porosity with curing A while BFSC concrete shows the lowest porosity with curing B. The value of porosity of concrete of FAC is highest ones with curing A due to the low pozzolanic of fly ash and the SRC concrete of curing B shows the highest result of the cumulative porosity. Therefore, for the same mix, both of curing method and type of used cementitious materials have a significant effect

on the porosity of concrete. The measured values of the cumulative porosity for all investigated concrete with two curing types are lower than the range reported by Raymond [3].

From data of Table 4, it is noticed that values of the cumulative pore surface area of concrete of curing A are higher than those of concrete of curing B. For both types of curing, the SF and FAC concretes indicate lowest and highest values of cumulative pore surface area, respectively. The results show that there is significant differences were detected between obtained results of the pore surface area due to change in both type of cement and curing method.

The real particle or pore size distribution must have maximum and minimum sizes. This was the physical interpretation associated with the use of reduced diameters and with the introduction of the upper and lower limits on the particle or pore size range [11]. The results showed that the maximum pore size is not evident where the corresponding density function approaches zero. This is because of the problem of mercury contact angle and the applied pressure, though no maximum size is explicitly defined. The applicable measured maximum pore diameters of OPC, SFC, FAC, and SRC concrete of curing B are larger than those of curing A while BFSC concrete of curing A indicates larger diameter than that of curing B. Further, SRC shows the smallest diameters for both of the curing ways. On the other hand, it is impossible to locate the real minimum pore size, based on the currently available mercury intrusion porosimetry data. It might not be valid to assume that the minimum size is negligible if smaller pores, for this reason, it should be reported that the values of minimum size existed in Table 4 are the smallest pore size which can be measured by MIP technique and this is not real minimum pore size.

The five concrete mixtures show very close results of average pore diameter with the two used types of curing. The concrete of curing A shows lower average pore diameter than that of concrete of curing B. From data of concrete of curing A, SFC mixture shows the highest average pore diameter and FAC concrete shows the lowest ones. While, concretes of curing B indicate that SRC mix has the highest average pore diameter and BFSC mix has the lowest ones.

6 Cumulative intrusion volume profiles

Cumulative intruded pore volume profiles for the investigated cementitious materials are provided in Figures 1, 2, 3, 4, and 5 for OPC, BFSC, SFC, FAC, and SRC, respectively. It is observed that the final intruded pore volumes for different types of the studied concretes can be regarded as very close, but the intrusion profiles shape varies slightly depending on the cement type and curing method. Concrete of curing A with pore size greater than $0.04\ \mu\text{m}$, OPC and SRC concretes indicate highest and lowest pore volume, respectively, while, for pore size smaller than $0.04\ \mu\text{m}$, FAC and SFC concretes show highest and lowest pore volume, respectively. Also, concretes of curing B indicate approximately the same pore volume for pore size larger than $10\ \mu\text{m}$, but for pore size ranged from 0.09 to $10\ \mu\text{m}$, BFSC concrete has the highest values and both of SRC and FAC show the lowest ones. SRC and OPC show larger pore volume than those of BFSC, SFC and OPC for the pore size less than $0.09\ \mu\text{m}$.

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From data of Table 3, and Table 4, it was concluded that, the presence of very fine particles of the cementitious materials lead to further pore refinement and through pore refinement and grain refinement, cementitious materials with ultrafine particle size or very high specific surface were able to cause substantial strength improvement in concrete. In the case of the pozzolanic admixtures, the pozzolanic reaction seems to cause a further improvement in the strength of concrete strength during the 28 days period.

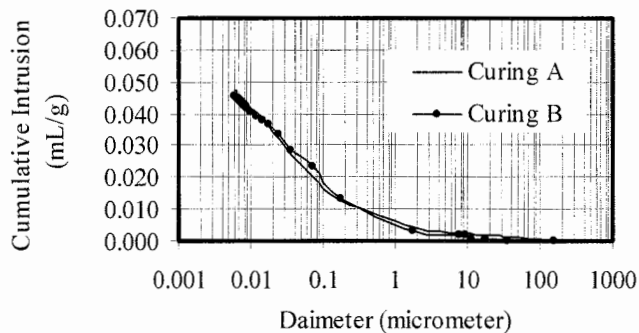


Figure 1 : Pore size distribution for OPC concrete mixture.

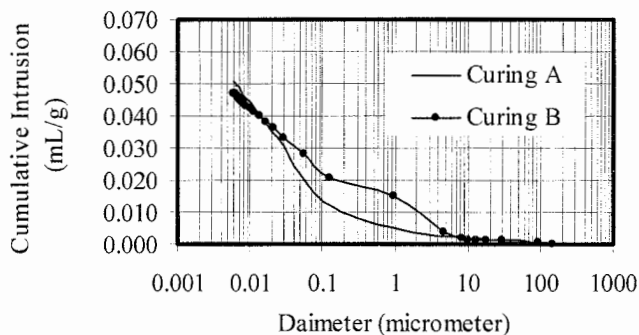


Figure 2 : Pore size distribution for BFSC concrete mixture.

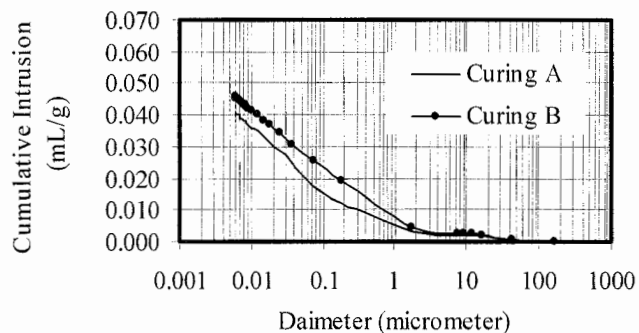


Figure 3 : Pore size distribution for SFC concrete mixture.

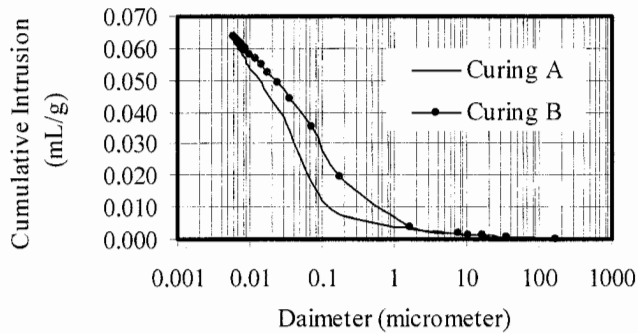


Figure 4 : Pore size distribution for FAC concrete mixture.

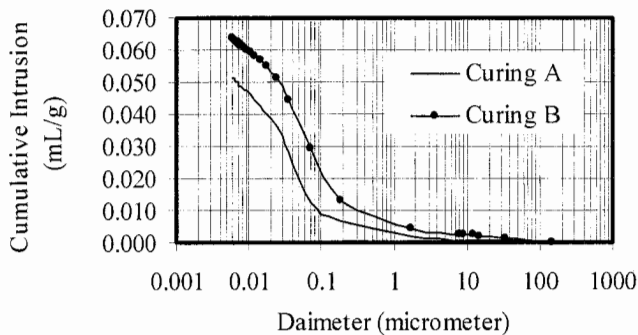


Figure 5 : Pore size distribution for SRC concrete mixture.

In this research, the concrete of curing A having smaller pore size than those of concrete of curing B and the strength values of the concrete of curing A are higher than those of concrete of curing B. The test results comply with the findings of Luping [12], he reported that for materials having the same matrix and porosity, the strength of material containing more large size pores is lower; even the strength of the material having lower porosity but containing more large size pores is lower than that of the concrete having higher porosity but comparatively less large size pores.

7 Conclusions

1. The incorporation of cementitious materials in concrete lead to a general enhancement in properties of both fresh and hardened concretes.
2. The pozzolanic reaction causes a further improvement in the concrete strength and the cement type plays a significant role in the produced concrete properties.
3. The obtained results demonstrate the importance of curing and confirm the fact that pore structure characteristics and pore size distribution are changed by both curing method and used cementitious materials.

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