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Influence of fly ash fineness and shape on the porosity and permeability of blended cement pastes

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Abstract: The effects of the fineness and shape of fly ash on the porosity and air permeability of cement pastes were investigated. Pulverized coal combustion (PCC) fly ash and fluidized bed coal combustion (FBC) fly ash classified into three different finenesses were used. River sand with particle size distribution similar to that of fly ash was also used for comparison. Portland cement was replaced with fly ash and ground sand at the dosages of 0, 20wt%, and 40wt%. A water-to-binder ratio (w/b) of 0.35 was used throughout the experiment. The results show that the porosity and air permeability of the pastes are influenced by the shape, fineness, and replacement level of fly ash. The porosity and air permeability of FBC fly ash pastes are higher than those of PCC fly ash pastes. This is due to the higher irregular shape and surface of FBC fly ash compared to the spherical shape and relatively smooth surface of PCC fly ash. The porosity increases with the increase in fly ash replacement level and decreases with the increase in its fineness. The permeability of PCC fly ash pastes decreases with the increase in replacement level and fineness, while for FBC fly ash, the permeability increases with the increase in replacement level. Decreases in porosity and permeability are due to a combined effect of the packing of fine particles and the reaction of fly ash.

Keywords: cement; fly ash; coal combustion; porosity; permeability

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1. Introduction

In designing concrete structures, durability is one of the most important properties to be considered, in addition to the ability of the structure to resist all loads. Concrete durability depends largely on fluids in form of liquid or gas migrating through hardened concrete. Concrete is a porous material; therefore, moisture movement can occur by flow, diffusion, or absorption. The ingress of various ions, liquid, and/or gas from the environment is responsible for deterioration and damage of concrete [1]. It is generally accepted that the pore structure and porosity of pastes, mortars, or concrete are among the most important properties and strongly affect both its mechanical properties (strength, creep, and shrinkage) and transport properties (permeability, diffusion, and absorption). Transport properties are intimately related to the resistance of concrete structures to various durability problems and controlled by the pore size distribution network of hardened cement pastes and concrete [2-3].

Fly ash is a pozzolanic material and a by-product from combustion of pulverized coal in an electricity power plant. Characteristics of fly ash vary due to coal type and combustion condition. In Thailand, it is estimated that since 2008, more than 3.5 million tons of fly ash has been produced annually. However, only half of this has been utilized. The majority of fly ash is from pulverized coal combustion from Mae Moh Power Station in the north. Recently, however, a

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number of fluidized bed coal combustion power plants have been put into service, and as a consequence, its fly ash is increasing. Utilization of this fly ash is still limited due to the lack of understanding on the characteristics of fly ash itself and the properties of fly ash concrete. Although many researchers investigated the influences of fly ash on the porosity and air permeability of blended cement pastes, few researchers were found dealing with the fineness and shape of fly ash and their influences on the properties of hardened cement pastes. Understanding the effects of the fineness and shape of fly ash on the porosity and air permeability of cement pastes will lead to an increasing use of fly ash in concrete.

2. Experimental

2.1. Materials

(1) Chemical composition. Portland cement type I (PC), pulverized coal combustion (PCC) fly ash from Mae Moh Power Station, fluidized bed coal combustion (FBC) fly ash from COCO Power Plant, and river sand were used. The chemical composition is listed in Table 1. The amounts of SiO_2, Al_2O_3, and Fe_2O_3 of PCC and FBC fly ashes are 81.54wt% and 75.92wt%, respectively. The SO_3 contents of PCC and FBC fly ashes are less than 5wt%, and the loss on ignition (LOI) is less than the limit of 6wt%. It is well established that classifying and grinding do not affect the chemical composition of fly ash [2, 4-7]. The main composition of river sand is SiO_2 with 91.3wt% [8].

(2) X-ray diffraction patterns. Fig. 1 shows XRD patterns of PCC and FBC fly ashes. PCC fly ash consists mainly of a glassy matrix with a relatively small amount of crystalline phases, such as quartz, mullite, and anhydrite. FBC fly ash, however, contains a higher percentage of crystalline materials, and the majority can be identified as quartz and anhydrite. This suggests that PCC fly ash should be slightly more reactive than FBC fly ash.

(3) Median particle size and surface area. Each type of fly ash was classified to three different finenesses, *viz*., coarse original, medium and fine fly ash. The median particle size (d_{50}) and surface area of all fly ashes are shown in Table 2. Particle size distribution was performed using a laser particle size analyser. The median particle size of PC is 14.1 μm which is the same as that of coarse FBC fly ash, while that of coarse PCC fly ash is slightly coarser at 18.7 μm. The median particle sizes of classified medium PCC fly ash and medium FBC fly ash are 6.4 and 7.0 μm, respectively. The median particle sizes of fine PCC fly ash and fine FBC fly ash are 2.2 and 2.4 μm, respectively. To study the packing effect, an inert material, *i.e*. river sand, was used to compare the results. The median particle size of coarse original river sand is quite large at 71.6 μm, whereas those of ground medium and fine sand are similar to those of fly ash at 7.0 and 3.3 μm.

Table 1. Chemical composition of cementitious materials wt%

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
PC	20.90	4.76	3.41	65.41	1.25	0.24	0.35	2.71	0.96
PCC fly ash	45.69	24.59	11.26	12.15	2.87	0.07	2.66	1.57	1.23
FBC fly ash	45.24	28.25	2.43	11.80	0.74	0.66	0.47	3.63	2.96
River sand	91.30	6.30	—	—	—	—	—	—	0.50

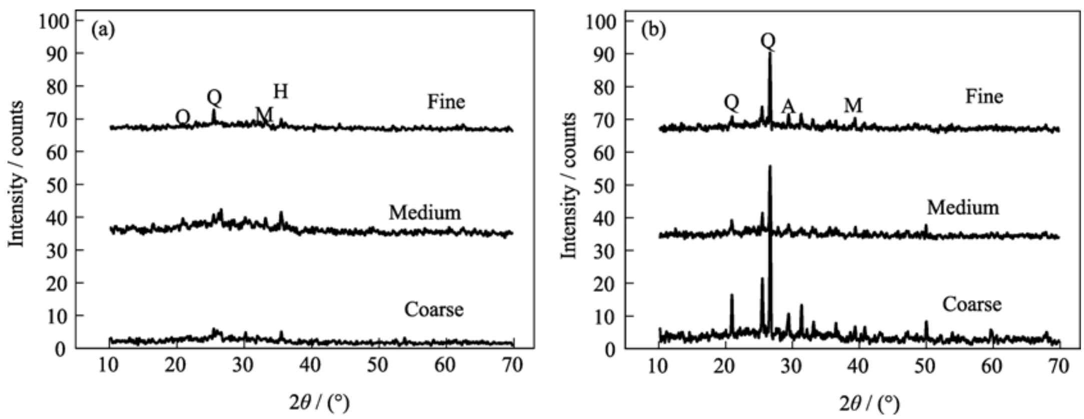

Fig. 1. XRD patterns of fly ash: (a) PCC; (b) FBC. Q—quartz; M—mullite; H—hematite; A—anhydrite.

Table 2. Median particle size and surface area of materials

Sample		Median Particle Size / μm	Specific Surface Area (Nitrogen Adsorption) / $(m^2 \cdot kg^{-1})$
PC		14.1	1300
PCC fly ash	Coarse	18.7	1650
	Medium	6.4	2100
	Fine	2.2	3150
FBC fly ash	Coarse	14.1	8200
	Medium	7.0	11200
	Fine	2.4	13250
River sand	Coarse	71.6	2050
	Medium	7.0	2700
	Fine	3.3	3250

Specific surface areas by nitrogen adsorption of PC, fly ash, and river sand are tabulated in Table 2. The specific surface area of PC is 1300 m^2/kg, while those of coarse PCC fly ash and coarse river sand are slightly higher at 1650 and 2050 m^2/kg, respectively. The specific surface area of coarse original FBC fly ash is, however, very high at 8200 m^2/kg. High specific surface area despite similar median particle size to that of PC suggests that its surface is irregular highly. Specific surface areas of the medium and fine fly ashes and ground river sand slightly increase with increasing fineness, as expected.

(4) Particle shape. Scanning electron microscope (SEM) images of powder materials are shown in Figs. 2 and 3. For PCC fly ash, coarse original fly ash contains mostly spherical particles with large particles. For classified medium and fine fly ashes, particles are spherical and smooth. For FBC fly ash, coarse, medium, and fine fly ashes all contain particles with highly irregular shapes and surfaces. This confirms the high specific areas of FBC fly ash. The difference in the shape of fly ash results from the difference in the coal burning process. The FBC system operates at a lower temperature in comparison to that of the PCC system. At high temperature, ash melts and forms spherical particles.

2.2. Mix proportion and preparation of samples

Fly ash and river sand were used to replace Portland cement at the dosages of 0, 20wt%, and 40wt%. A constant water-to-binder ratio (w/b) of 0.35 was maintained in this study. Cylindrical paste specimens with 38 mm in diameter and 65 mm in height were cast for porosity and air permeability tests. After being cured in saturated lime water for 28 and 90 d, the ends of samples were cut with a diamond saw to obtain 50-mm-high cylinders. Samples were then dried in an oven at 105±5°C for approximately 24 h until constant weight was reached and kept in a dessicator with silica gel for cooling for another 24 h [9-11].

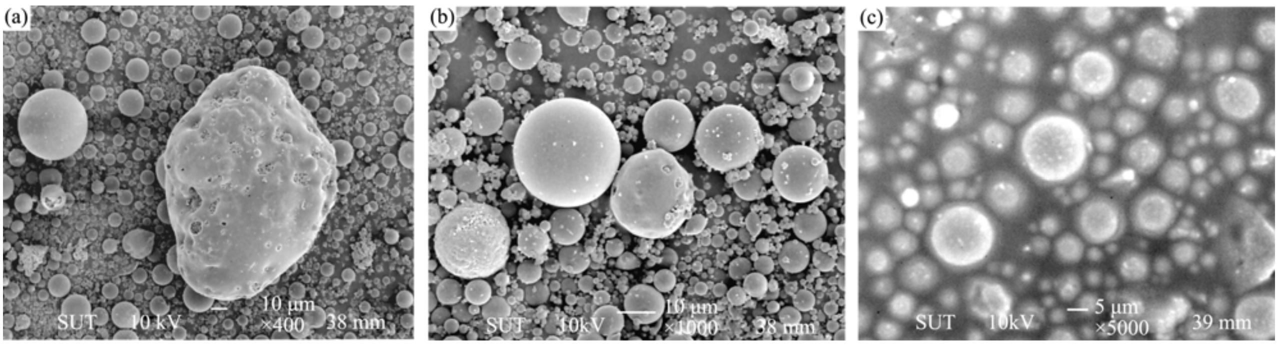

Fig. 2. Particle shapes of PCC fly ash: (a) coarse; (b) medium; (c) fine.

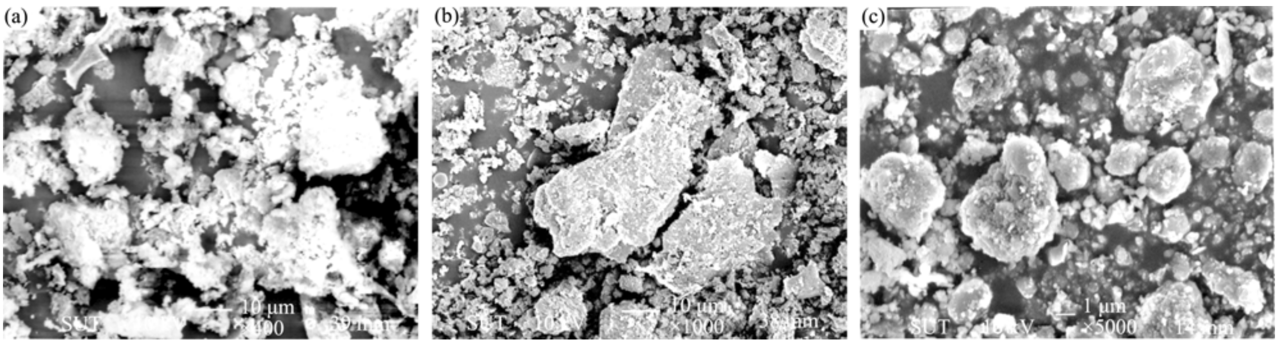

Fig. 3. Particle shapes of FBC fly ash: (a) coarse; (b) medium; (c) fine.

2.3. Porosity determination by helium

The porosity (P) of the pastes was performed using a helium porosimeter with dried paste samples. The porosity was determined by a combination of three physical properties, *viz*., grain volume (V_g), bulk volume (V_b), and pore volume (V_p). The grain volume and pore volume were determined from helium injection by passing helium through the specimen. The bulk volume was calculated from the relationship between the length and the diameter of the specimen. The relationships among them are as follows:

$V_g=V_b-V_g$,

$P=V_g/V_b\times100\%$.

2.4. Air permeability

Although there are no standards for gas permeability tests, a method by which air flow is used to determine the intrinsic permeability of rock is available in ASTM standard D4525. A cell permeameter as shown in Fig. 4 based on equipment used successfully in petroleum technology to measure the permeability of rock cores was used.

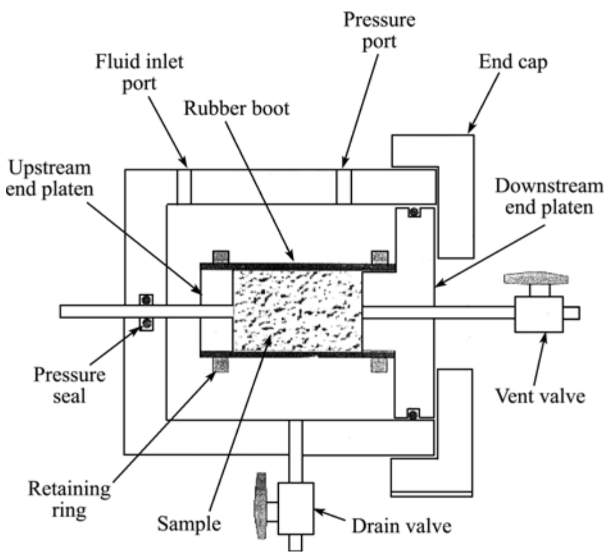

Fig. 4. Cell and specimen holder.

To determine the permeability of the sample, air at a known initial pressure (upstream pressure) was applied to force air to flow through the length of the sample. The sample was sealed along its length. The flow rate of air out of the other end of the sample was measured. The permeability of the sample was calculated using Darcy's law through the knowledge of upstream pressure, flow rate during test, atmospheric pressure, air viscosity, and the length and cross section of the sample. The following equation in a form of Darcy's law is used to calculate permeability. All pressures need to be in units of atmospheres (atm):

$$K=\frac{2Q_e P_e \mu L}{\left(P_i^2-P_e^2\right)A},$$

where, K is the coefficient of permeability, m^2 (10^2 darcy); Q_e the exit flow rate of air, m^3/s; P_e the exit pressure of air, Pa; L the length of the plug, m; A the cross-sectional area of the specimen, m^2 ; P_i the entrance pressure of air, Pa; μ the viscosity of air at test temperature, Pa·s.

Due to gas slippage, it was not accurate to determine intrinsic permeability as an average of calculated K values of different inlet pressures. Therefore, a regression method was applied to obtain the correct intrinsic permeability [12-16]. Using regression analysis, the relationship between gas permeability and the reciprocal of mean pressure ($1/P_m$, where $P_m=(P_i+P_{atm})/2$) was determined. The coefficient b of the equation $K=a(1/P_m)+b$ gives the correct value of gas intrinsic permeability (K_g), as shown in Fig. 5.

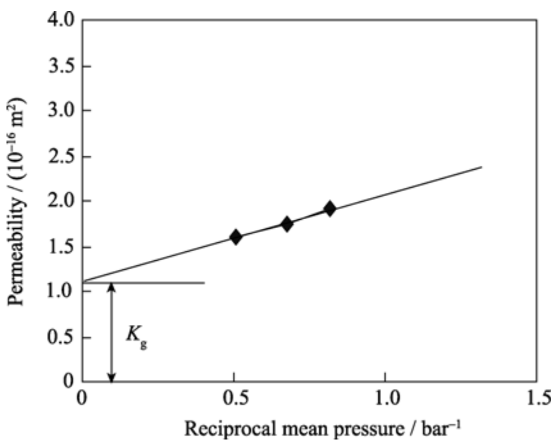

Fig. 5. Relationship between permeability and reciprocal mean pressure.

3. Results and discussion

3.1. Effect of fly ash on the porosity and permeability of the pastes

3.1.1. Porosity determination

Results of porosity of the pastes are plotted in Figs. 6-8. As anticipated, the porosity of coarser fly ash pastes increased with the increase in fly ash replacement level. The porosity of the pastes containing finer fly ash is significantly lower than that of coarser fly ash at all replacement levels and ages, and this conforms to the results of Chindaprasirt *et al*. [17]. For example, the porosities of coarse PCC fly ash pastes with 20wt% replacement at 28 and 90 d are 26.0% and 23.0%, respectively. Whereas the porosities of medium and fine PCC fly ash pastes are 25.1% and 20.0% at 28 d and 21.2% and 19.8% at 90 d (Fig. 6).

Results of FBC fly ash pastes show a similar trend to those of PCC fly ash pastes (Fig. 7). Decrease in porosity is mainly a result of the use of classified fine fly ash. The porosity of FBC fly ash pastes is higher than that of PCC fly ash pastes due mainly to the difference in particle morphology. The shape and surface of FBC fly ash are highly irregular since they are formed at low temperature of the fluidized bed combustion system, while those of PCC fly ash are spherical and the ash has a relatively smooth surface due to high-temperature combustion.

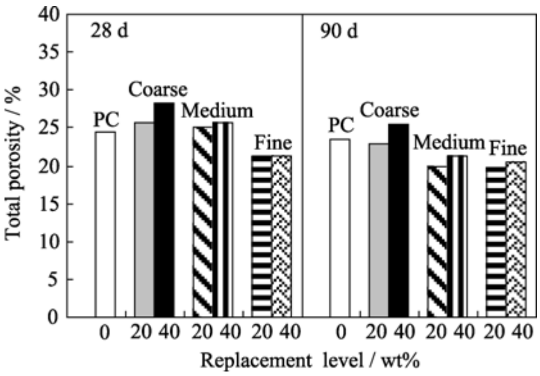

Fig. 6. Porosity of PC pastes and PCC fly ash pastes at 28 and 90 d with w/b=0.35.

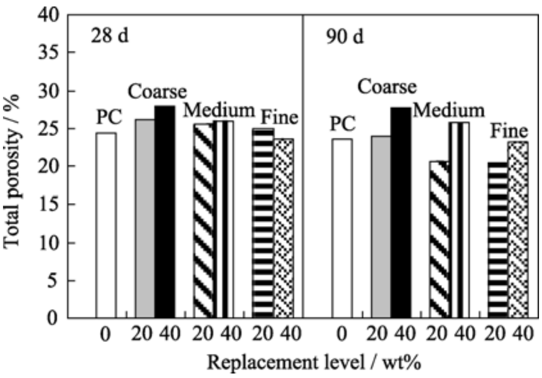

Fig. 7. Porosity of PC pastes and FBC fly ash pastes at 28 and 90 d with w/b = 0.35.

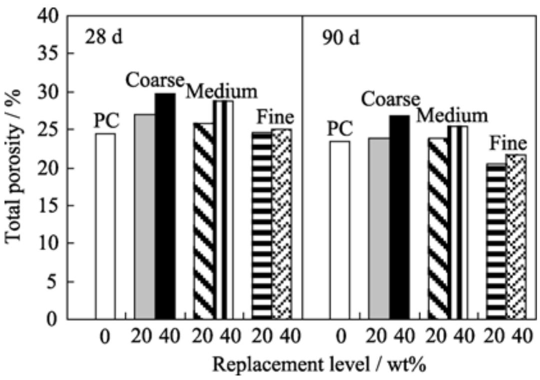

Fig. 8. Porosity of PC pastes and river sand pastes at 28 and 90 d with w/b=0.35.

Pozzolanic reaction of classified fine fly ash was faster than that of coarser original fly ash. In addition, fine fly ash particles also produced dispersing and packing effects resulting in a more homogeneous and denser matrix [7]. Fly ash particles increased the available space around cement particles and accelerated hydration reaction. The mechanisms of reducing the porosity of fly ash pastes, thus, consisted of hydration, pozzolanic reaction, and dispersing and packing effects.

3.1.2. Air permeability of the pastes

Results of air permeability of the pastes are shown in Figs. 9-11. As usual, the air permeability of all pastes decreases with curing time as the capillary pores are gradually reduced resulting from hydration and pozzolanic reactions. It can be observed that incorporation of PCC fly ash significantly improved the air impermeability of the pastes with the increases in fly ash fineness and replacement levels. For example, at 90 d, the permeabilities of coarse PCC fly ash at 20wt% and 40wt% replacements are 0.54×10^{-16} and 0.48×10^{-16} m^2, while those of medium and fine PCC fly ash pastes at 40wt% replacement level are 0.38×10^{-16} and 0.31×10^{-16} m^2 (Fig. 9). It has been suggested by Bakker [18] that the presence of fly ash leads to a greater precipitation of cement gel products in comparison to that of PC alone. This results in an effective blocking of pores and, thus, helps in reducing permeability. In addition, pozzolanic reaction of fly ash generates additional cementitious compounds that block channels, and fill pore space and, thus, further reduce the permeability of the hardened pastes. The fineness of fly ash is a primary physical characteristic that influences the pozzolanic activity. The glass content of fine fly ash particles is higher than that of coarser ones from the same source [6]. When fine fly ash is incorporated, the pastes are more homogeneous and denser as a result of pozzolanic reaction and packing effects; the air permeability of the pastes is, therefore, decreased.

Results of FBC fly ash pastes as shown in Fig. 10 indicate that air permeability of FBC fly ash pastes showed a similar trend to those of PCC fly ash pastes. The air permeability of FBC fly ash pastes also decreases with the increase in fineness of fly ash. Reduction in air permeability

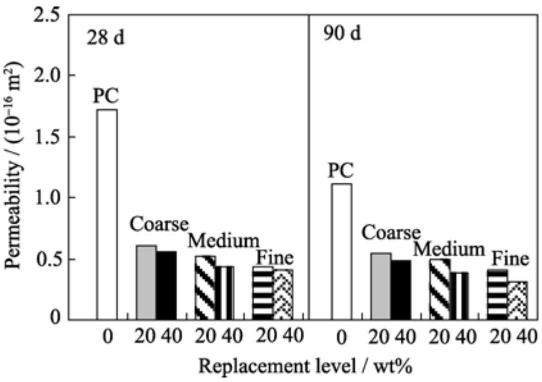

Fig. 9. Permeability of PC pastes and PCC fly ash pastes at 28 and 90 d with w/b = 0.35.

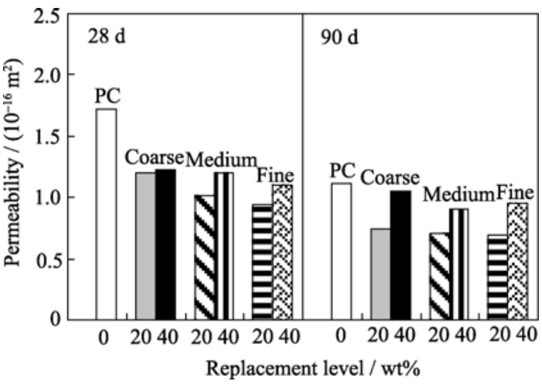

Fig. 10. Permeability of PC pastes and FBC fly ash pastes at 28 and 90 d with w/b=0.35.

as a result of incorporation of FBC fly ash is lower than that of PCC fly ash. The decrease was associated with a decrease in total porosity of the pastes. At the age of 90 d, the air permeabilities of coarse, medium, and fine FBC pastes at 20wt% replacement levels are 0.74×10^{-16}, 0.70×10^{-16} and 0.69×10^{-16} m^2, while those of corresponding PCC fly ash pastes are 0.54×10^{-16}, 0.48×10^{-16} and 0.41×10^{-16} m^2. This is due to the shape and crystalline phase of fly ash. The spherical shape of PCC fly ash provided good distribution of particles and enhances nucleation in comparison to highly irregular shaped FBC fly ash. In addition, FBC fly ash has a higher content of crystalline phase and should result in a lower pozzolanic reaction compared with PCC fly ash at the same fineness.

3.2. Effect of river sand on the porosity and permeability of the pastes

3.2.1. Porosity determination

The porosity of the pastes with river sand is determined to compare packing and pozzolanic reaction effects with those of fly ash pastes, as shown in Fig. 8. The porosity of river sand pastes decreased with curing time and sand fineness. The porosities of coarse river sand pastes with 20wt% replacement levels at 28 and 90 d are 27.0% and 23.9%, respectively. The porosities of medium and fine sand pastes at 90 d are 23.9% and 20.5%. Reduction in porosity of the pastes is contributed to cement hydration and packing effects of a small particle of ground river sand. The porosities of river sand pastes are, however, slightly higher than those of fly ash pastes. The differences are more noticeable with PCC fly ash pastes, indicating that porosities of PCC fly ash reduce as a result of both pozzolanic reaction and packing effects, while incorporation of river sand decreases the porosity of the pastes from the packing of small sand particles.

3.2.2. Air permeability of the pastes

Results of air permeability of river sand pastes at 28 and 90 d are shown in Fig. 11. The permeability reduces with the increases in curing time and sand fineness. The permeabilities of river sand pastes with 20wt% replacement level at 28 and 90 d are 0.79×10^{-16}, 0.65×10^{-16}, 0.52×10^{-16} m^2, and 0.59×10^{-16}, 0.57×10^{-16}, 0.44×10^{-16} m^2, respectively. Reduction in air permeability is due to hydration of cement and the packing effect of sand particles. The permeability of river sand pastes is higher than that of corresponding PCC fly ash pastes due to pozzolanic reaction of PCC fly ash as well as its spherical and smooth surface. The permeability of FBC fly ash pastes is, however, slightly higher than that of river sand pastes, suggesting that its pozzolanic reaction is relatively slow, and its highly irregular shape and surface are not suited for dispersing and packing effects. The smooth and spherical shape of PCC fly ash can fill more pores than the irregular shape of ground river sand. The highly irregular shape of FBC fly ash results in the lowest degree of pore filling.

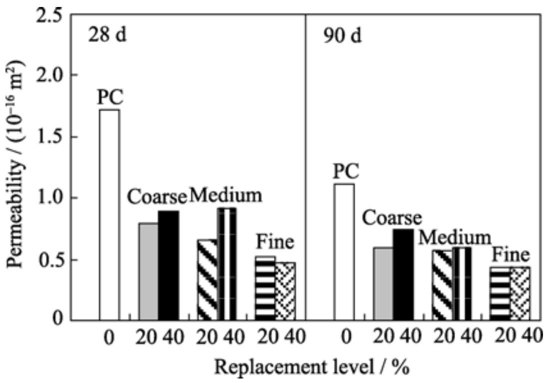

Fig. 11. Permeability of PC pastes and river sand paste at 28 and 90 d with w/b = 0.35.

3.2.3. Relationship between porosity and air permeability of the pastes

Fig. 12 shows relationships between porosity and air permeability of the pastes. Air permeabilities of the pastes decrease with decrease in porosity. The air permeability of FBC fly ash pastes is significantly larger than those of river sand and PCC fly ash pastes. The permeability of river sand is slightly larger than that of PCC fly ash. The spherical particle shape of PCC fly ash produces a good dispersing of solid particles and filling of pores. The relatively low permeability of river sand pastes is a result of the filling of voids of sand. With the angular shape, sand particles fill voids reasonably well but not as good as PCC fly ash. FBC fly ash with a highly irregular shape and surface produces the lowest degree of packing or filling of voids, which results in relatively high permeability of the pastes. In addition, incorporation of fly ash produces pozzolanic reaction, which will help filling voids and a lower permeability of the pastes. PCC fly ash is more reactive and can reduce the permeability compared with FBC fly ash.

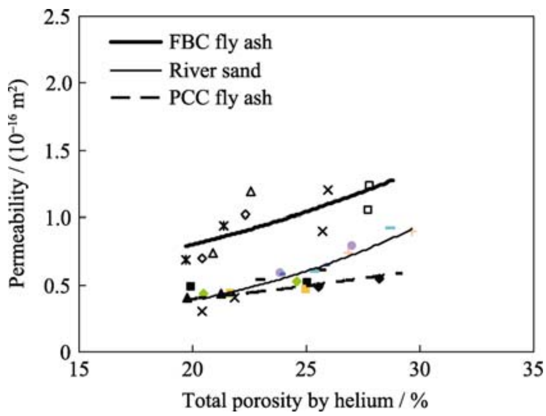

Fig. 12. Relationship between porosity by helium and permeability of the pastes at a w/b ratio of 0.35

4. Conclusions

(1) The porosity and air permeability of the pastes are influenced by the curing time and incorporation of fine materials. Reductions in porosity and air permeability of the pastes with increasing curing time are a result of the increase in hydration of cement. Influences of the incorporation of fine materials are related to particle shape, fineness, replacement level, and degree of pozzolanic activity.

(2) The air permeability of FBC fly ash pastes is higher than those of river sand and PCC fly ash pastes at the same porosity. This is due primarily to the highly irregular shape and surface of FBC fly ash, as it is from fluidized bed combustion and the burning temperature is relatively low. The incorporation of FBC fly ash, therefore, produces a low degree of packing.

(3) PCC fly ash is from conventional pulverized coal combustion and consists of spherical and relatively smooth surface particles and, thus, produces a good packing of fine particles. The relatively low permeability of river sand pastes is from a reasonably good packing of fine sand particles.

(4) The pozzolanic activity of fly ash further reduces the permeability and porosity of fly ash pastes. The pozzolanic reactivity of FBC fly ash is low in comparison to that of PCC fly ash and, thus, marginally improves the porosity and permeability of the pastes. The pozzolanic reactivity of PCC and FBC fly ashes also increases with the increase in their finenesses. This contributes to lower porosity and permeability, as the pozzolanic activity of fine fly ash is greater than that of the coarser one. Decreases in porosity and permeability are due to a combined effect of the packing of fine particles, the pozzolanic reaction of fly ash, and the hydration of cement.

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