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PORE SIZE DISTRIBUTION OF METAKAOLIN PASTE

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ABSTRACT

The porosity and pore size distribution of cured OPC-metakaolin paste has been investigated. Pastes containing 0,5,10 and 15% metakaolin were prepared at a constant water/binder (w/b) ratio of 0.55. Specimens were moist cured for periods from 3 to 365 days. The intruded pore volume and the pore structure were determined by mercury intrusion porosimetry. The proportion of large pores (radius > 0.02 mm) in the paste decreases with both increase in metakaolin content and increase in curing time. Although the total intruded pore volume generally decreases with increase in curing time it is found to increase with increase in metakaolin content. Also an increase in pore volume is observed between the curing times of 14 and 28 days for pastes containing metakaolin. This latter observation is explained in terms of two possible mechanisms.

Introduction

The partial replacement of ordinary Portland cement with pozzolanic materials can be advantageous, in that it can increase the durability of paste, mortar or concrete if the proper curing regime is adopted. This is due to the fact that the calcium hydroxide produced by the cement hydration reacts with the pozzolan and produces additional gel which has a pore blocking effect and therefore alters the pore structure and the strength. In addition there is a reduction in calcium hydroxide (CH) which leads to improved resistance to sulphate attack and alkali-silica reaction. Various pozzolanic materials such as fly ash and condensed silica fume have been used to partially replace cement. Recently metakaolin which is an ultra-fine pozzolan produced from calcined clay has been added to the list of pozzolanic materials [1-8]. Metakaolin resembles silica fume in some respects, particularly in terms of its very large surface area (>12,000 m^2/kg) and also that it is a silica based product, which on reaction with CH produces C-S-H gel. However, metakaolin also contains alumina which on reaction produces additional alumina containing phases some of which are crystalline. These include C_4AH_{13}, C_2ASH_8 and C_3AH_6 [1,9-12].

When mineral admixtures such as silica fume and rice husk ash are blended with cement, the total porosity of the paste is generally reduced and a finer pore structure develops relative to that in pure OPC paste. Also, there are equivalent reductions in permeability [13]. For example, a recent paper by Durekovic [14] on OPC-CSF pastes of low w/b ratio (0.28) shows that pore volumes decrease systematically with increase in curing time and also generally decrease with increase in CSF content. Fly ash (PFA) however, appears to be anomalous [13] in this respect as OPC-PFA blends produce (other than at very long curing times) higher porosities and a coarser pore structure than the control paste even though permeability is reduced. However, this is explained in terms of the development of fragile barriers separating large pores which reduce permeability but which are destroyed by the high pressures employed in mercury porosimetry.

In the case of cement replacement by metakaolin, Bredy et al. [1] also report an increase in the total porosity of OPC-metakaolin pastes (relative to pure OPC paste) for metakaolin contents in excess of 20% at a curing period of 28 days. From their porosimetry data they discount any collapse of the internal microstructure and attribute the phenomenon to the "filler effect" of the fine metakaolin particles. However, interpretation of their data is unclear and compounded by the fact that they used increasing w/b ratios with increasing metakaolin content.

In the current work, a detailed study is made of the porosity and pore size distribution of pastes with 0%, 5%, 10% and 15% replacement of cement with metakaolin at a w/b ratio of 0.55. Mercury intrusion porosimetry was used to determine porosity and pore size distribution. The pastes were moist cured at 20 ± 1°C for 3,7,14,28,90 and 365 days. The purpose of this investigation is to gain a fundamental understanding of the influence that metakaolin has on the porosity and pore structure of cement paste.

Experimental

Materials and Mix Proportions. Ordinary Portland cement was used. Metakaolin was supplied by ECC International under the commercial name Metastar. The major constituents of the metakaolin were SiO_2 (52.1%), Al_2O_3 (41.0%) and Fe_2O_3 (4.32%); the surface area of the metakaolin was 12000 m^2/kg. Further details about the materials are given in reference [15].

Four different pastes were prepared, a control paste and pastes in which the OPC was partially replaced (by mass) with respectively 5,10 and 15% metakaolin. The w/b ratio was 0.55.

Specimen Preparation and Curing. The pastes were cast in steel moulds of dimensions 100mm × 100mm × 100mm and moist cured at 20 ± 2°C for periods of 3,7,14,28,90 and 365 days. Moist curing consisted of wrapping the specimens with cling film and placing in plastic bags [15]. After the required period of curing, paste samples of up to 5g mass were taken from the middle central region of each cube and dried in a sealed cabinet at 40°C under silica gel. This moderate form of drying was chosen to avoid possible decomposition of any metastable phase which may be formed and to prevent possible disruption of the microstructure. Loss in mass was very rapid and normally 85% of the water was lost within the first 24 hours.When samples reached constant mass (normally within 48 hours), they were stored in an air tight container. The samples were broken further (1-2 g mass) and were subsequently used for mercury intrusion porosimetry testing. The cube strengths and CH content of the cured pastes are reported elsewhere[15].

Mercury Intrusion Porosimetry. Two Fisons (Italy) instruments were used for mercury intrusion porosimetry, the Macropore Unit 120 and the Porosimeter 2000WS. The macropore unit is used to fill the dilatometer containing the sample with mercury under vacuum at

100 KPa. It also allows the macropore measurements to be performed by releasing the vacuum pressure slowly and noting the intruded volume at each pressure increment. The macropore measurements are complete when the pressure reaches atmospheric pressure. The Porosimeter 2000WS is used to perform the high pressure measurements and has a capacity of 200 MPa (2000 bars). It can measure pores with radii down to 0.004 µm. The Washburn equation [16] was used to calculate the pore radii. The contact angle between the mercury and the pore wall of the paste was taken as 140°.

Results and Discussion

The total intruded pore volume versus curing time for all pastes is shown in Figure 1. For the control paste there is a continuous reduction in total pore volume with age and also the rate of reduction declines with age. For pastes containing metakaolin, total pore volume also decreases (up to 14 days) but at an increasing rate. Then between 14 and 28 days pore volume actually increases. Beyond 28 days pore volume again continues to decrease with age, but at a decreasing rate. Thus there is a clearly defined minimum point at around 14 days for pastes containing metakaolin. Also these pastes possess a greater total pore volume than the control paste. It is of significance to note that this minimum in total pore volume at 14 days coincides with a maximum in relative strength and a minimum in CH content previously reported by the authors [15] for these specimens. Thus, the increase in pore volume between 14 and 28 days appears to be associated with a renewed increase in CH content and a decline in relative strength.

Figure 2 shows the threshold radius for pastes with and without metakaolin at different curing periods. The threshold radius is taken as the radius before which the cumulative pore volume rises sharply. In some pastes containing metakaolin, the threshold radius was not always easy to determine because the cumulative curves showed the development of two distinct pore size populations, a large population at very fine pore sizes and a much smaller population at somewhat coarser pore sizes. This produces a step in the cumulative pore volume versus pore radius curve (see Figure 3b) which is not present for the control paste (see Figure 3a). The way in which the threshold radius was located is illustrated in the two figures. It is clear from Figure 2 that the threshold radius falls very rapidly with curing time within the first few days whereas beyond 28 days it gradually approaches a constant value. There is also a decrease in threshold radius with increase in metakaolin replacement level confirming that a finer pore structure is obtained with metakaolin present. It is also important to note that there is not much difference in threshold radius for the 10% and 15% metakaolin pastes beyond the age of 14 days.

The effect which metakaolin has on the pore size distribution within the total pore volume, for pore sizes less than 20nm (micropores) and pore sizes greater than 20nm (macropores) at different curing times is illustrated respectively in Figures 4a and 4b. The figures plot the percentage of the total pore volume less than or greater than 20nm against curing time. For both plots, the control paste shows a smooth continuous curve. In contrast, the curves for the pastes with metakaolin show a discontinuity at around 14 days. This discontinuity results from the fact that for pastes containing metakaolin the proportion of porosity in the 'micropore' region increases sharply up to 14 days and then either levels off or shows a small reduction. This corresponds with the increase in total pore volume between 14 and 28 days shown in Figure 1. Thus the renewed increase in CH content between 14 and 28

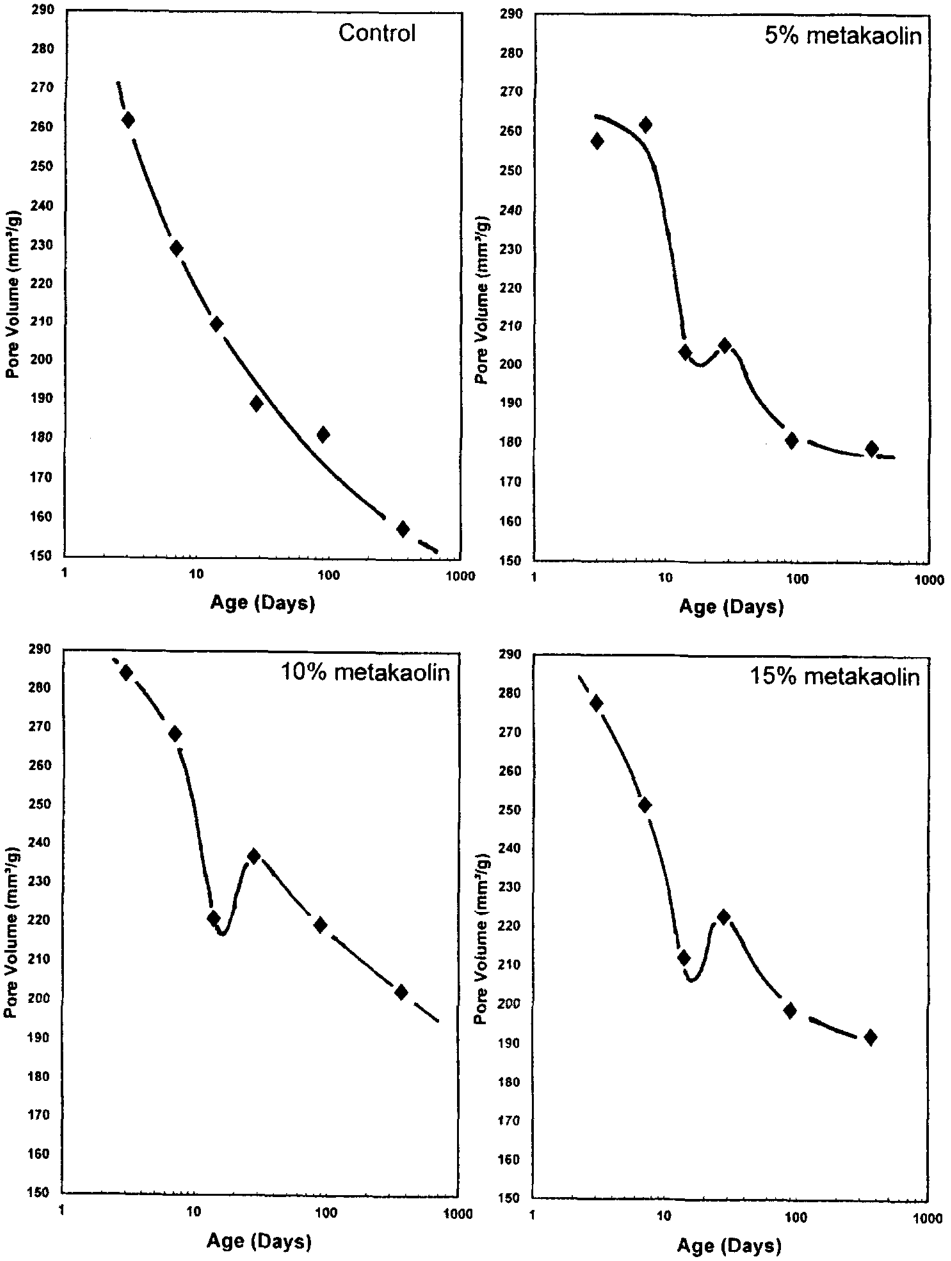

FIG. 1.
Total intruded pore volume versus curing time for OPC-metakaolin pastes.

days mentioned previously also appears to be linked to a termination of the pore refinement process and a tendency for the proportion of ultra-fine porosity to decrease and conversely for the coarser porosity to increase. The figures also clearly illustrate the effect which increasing levels of metakaolin have on refinement of the pore structure.

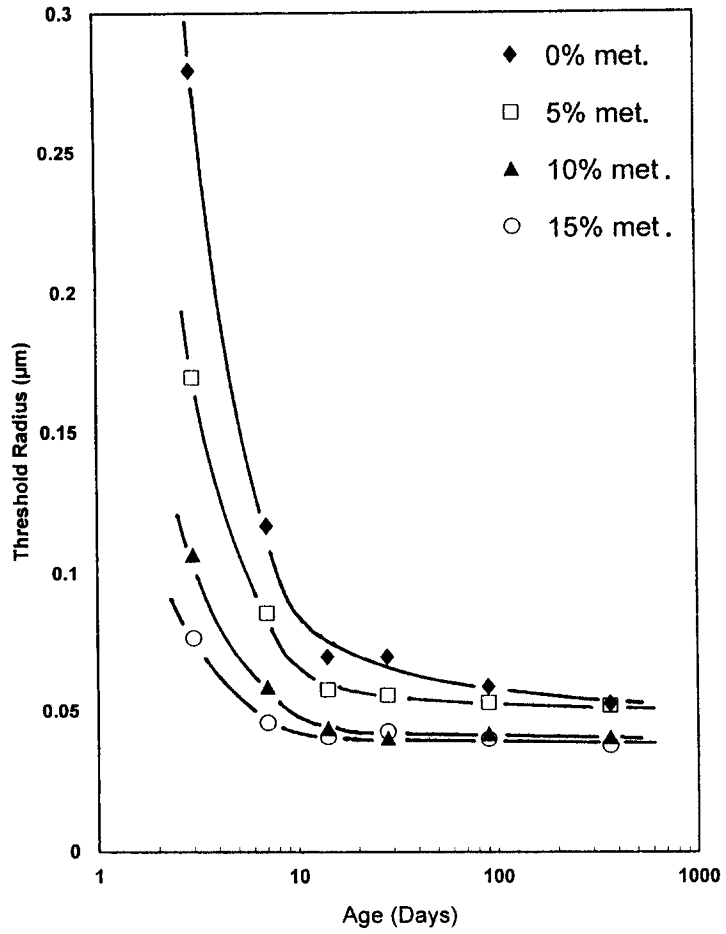

FIG 2
Threshold radius versus curing time for OPC-metakaolin pastes.

There is no doubt from the observations made that increasing levels of replacement of cement with metakaolin (up to 15% replacement) produce a general refinement of the pore structure of the paste. However, in contrast to the cement paste, the refinement process appears to terminate at 14 days and this corresponds with a maximum in relative strength, a subsequent small increase in total pore volume and a renewed increase in CH level. There are a number of possible explanations for these phenomena:

i. Formation by about 14 days,of an inhibiting layer of reaction product around the metakaolin particles, thus terminating their reaction with CH and preventing further formation of 'pore blocking' gel. Hence, the coarser pores formed by dissolution of CH crystals reported by a number of workers [17] can no longer be blocked off by further gel formation.

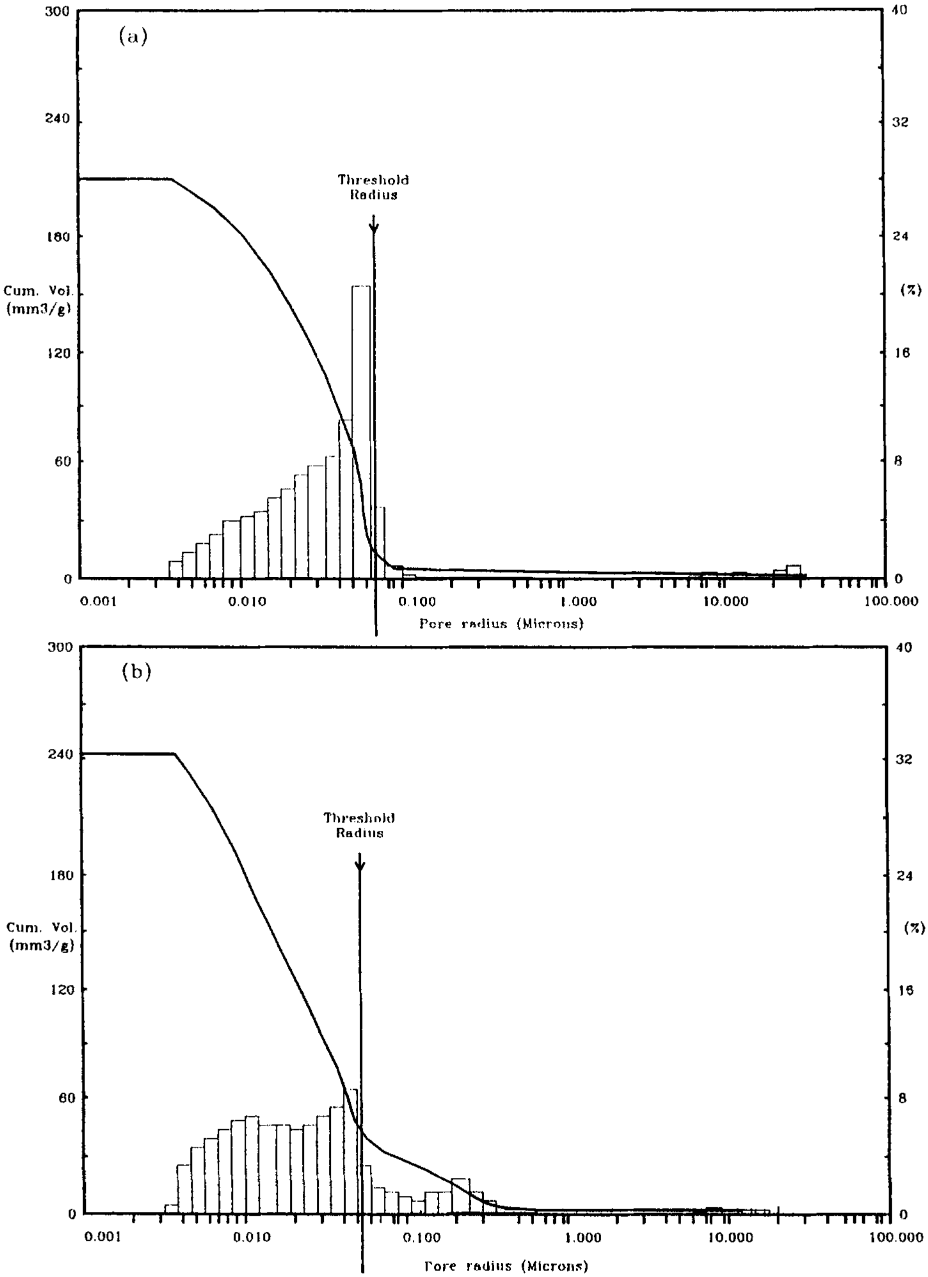

FIG. 3.
Determination of threshold radius for a) OPC paste cured for 14 days and b) OPC-10% metakaolin paste cured for 14 days.

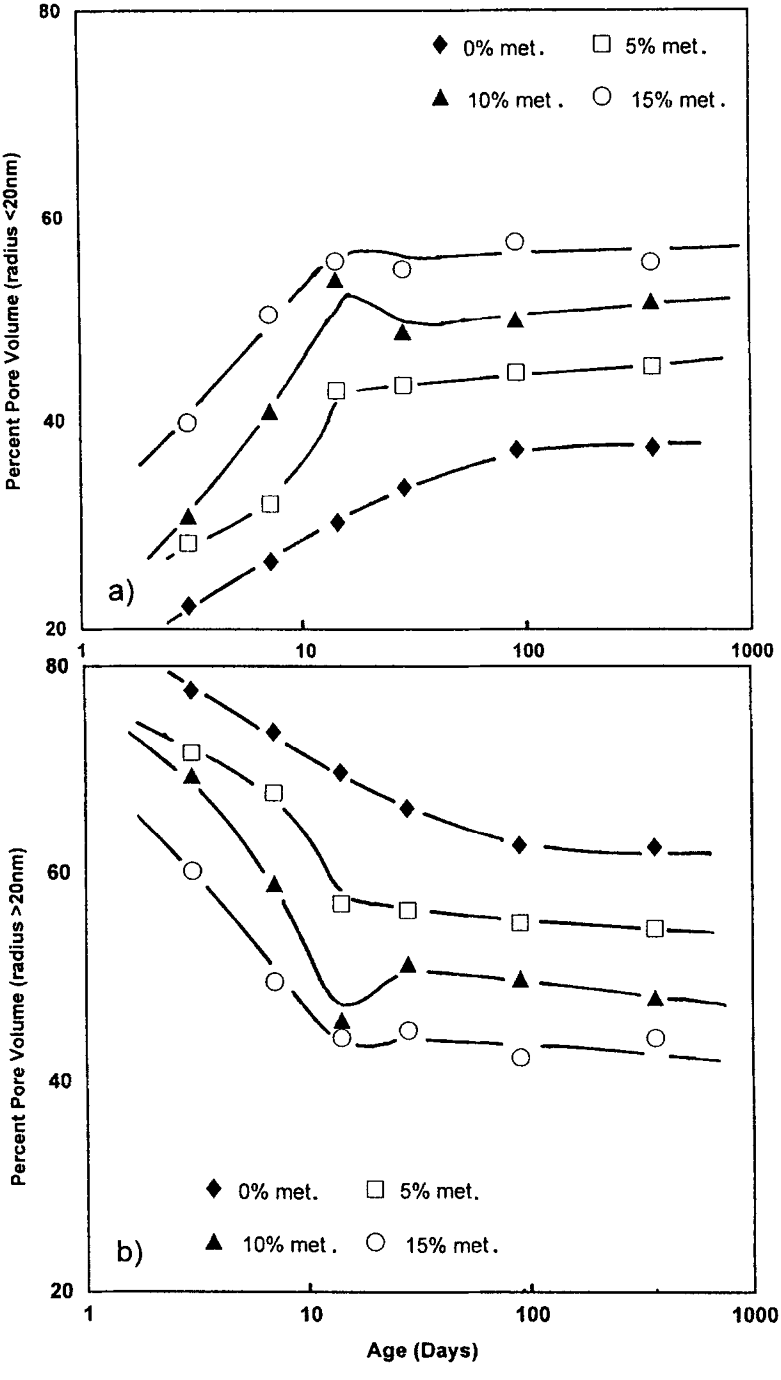

FIG. 4.
Pore size distribution versus curing time for a) radii<20nm and b) radii>20nm of pastes.

ii. Activation of a phase transformation of reaction products possibly as a result of the changing CH/metakaolin ratio with age. De Silva and Glasser [10] reported such a transformation in compacted 1:1 (by weight) mixes of metakaolin and CH moist cured at 40°C. The initial reaction products are C-S-H gel, C_4AH_{13} and C_2ASH_8 and subsequently hydrogarnet (C_2ASH_8) appears. It is suggested by the authors that there is a transformation from the less dense C_2ASH_8 and C_4AH_{13} to dense hydrogarnet and that this transformation is associated with a decrease in solid volume and hence an increase in porosity and no further increase in strength.

There is no reason why both processes cannot operate simultaneously. However, more detailed analytical work is required to identify the actual mechanism.

Conclusions

The incorporation of metakaolin in cement paste leads to refinement of the pore structure. The threshold value for paste decreases as the metakaolin content in the paste increases. The proportion of pores with radii smaller than 20nm is increased as the replacement level of cement by metakaolin increases. Total intruded pore volumes increase between the ages of 14 and 28 days for metakaolin paste.

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