Pergamon

Cement and Concrete Research 31 (2001) 1653–1654

CEMENT AND CONCRETE RESEARCH

Discussion

A discussion of the paper "Mercury porosimetry—an inappropriate method for the measurement of pore size distributions in cement-based materials" by S. Diamond[☆]

Stan Wild*

School of Technology, University of Glamorgan, Pontypridd, Mid Glamorgan, Wales CF37 1DL, UK

Received 12 February 2000

Sidney Diamond, in his paper on the limitations of mercury porosimetry in determining pore size distributions in cement-based materials [1], very effectively articulated what most people using the technique for this purpose already knew or at least suspected. This in no way detracts from the very eloquent way in which the author presented, in a convincing manner, the available evidence to demonstrate that the pore size distributions, obtained from mercury porosimetry of cement-based systems, considerably overestimate the volume of fine capillary pores and underestimate the volume of coarse capillary pores. That is, the cumulative pore volume versus pore diameter curves are much steeper than they ought to be and are shifted by one or two orders of magnitude to finer pore sizes.

As Diamond points out, the capillary pores are in practice not cylindrical with fixed diameters but consist of long percolative chains made up of pores of various sizes. Along these pore chains will be constrictions, which Diamond calls "choke points," where the pore diameter is very narrow. Diamond equates the pore diameter at the "choke points" with the threshold radius and presents evidence to show that when the mercury pressure is sufficient to allow "Darcy flow" through these constrictions, a large proportion of the whole pore system is simultaneously intruded, which produces a very steeply rising cumulative pore volume versus pore diameter curve. This will of course still exclude pores finer than the threshold diameter or pores linked by constrictions finer than the threshold diameter. These very fine pores will include "gel pores," which are assumed to have diameters of the order of 1–3 nm [2] and require entry mercury pressures in excess of most commercial porosimeters.

This interpretation indicates that within a paste of a given w/c ratio and age the "choke points" exhibit a relatively limited range of diameters as they appear to be intruded over a rather limited mercury pressure range. The capillary pore structure, including the size of the "choke points," is a function of the initial cement particle size distribution, the w/c ratio and the age of the paste. Thus, the initial size of the "choke points" will reflect the closest approach of cement particles which will decrease with decrease in w/c ratio. These "choke points" will gradually narrow with age as the cement hydrates, due to gel formation and autogenous shrinkage, and some of the pore volume may become totally isolated by gel. Hence, the threshold radius will decrease with increase in curing time and decrease in w/c ratio as observed by numerous authors, Cook and Hover being a recent example [3]. Therefore, although the pore size distribution calculated from the mercury intrusion is not a true reflection of the actual pore size distribution in the paste, the decreasing threshold radius very effectively reflects the increasing pore refinement within the paste. Thus, as long as these limitations are taken into account in interpreting results, the technique is still a very valuable technique particularly in making comparative assessments of the pore refinement that is taking place within a given system. An example of this would be where cement is being replaced by different pozzolans.

Khatib and Wild [4] employed mercury porosimetry to follow the pore refinement with time of pastes in which increasing amounts of PC were replaced by metakaolin. Pore refinement was indicated by a continuous decrease in threshold diameter with increasing age and also a systematic decrease in threshold diameter with increasing metakaolin content. To reinforce the evidence for pore refinement, data were also presented as plots of the percentage of the total pore volume that is intruded at pore radii below an arbitrary value of 20 nm (diameter 40 nm)

[☆] Cem. Concr. Res. 30 (2000) 1517–1525.

* Tel.: +44-3-482-142; fax: +44-3-482-250.
E-mail address: swild@glam.ac.uk (S. Wild).

PII: S0008-8846(01)00616-0

versus age. In retrospect and in light of Diamond' s paper, this is just another way of illustrating the change in threshold diameter. If the arbitrary value of pore diameter is chosen to lie between the threshold diameter for the Portland cement paste and the minimum threshold diameter for the Portland cement–pozzolan blends (normally the highest substitution level), then as the substitution level increases (or also as curing time increases) the cumulative pore volume versus pore diameter curve will shift to the left (lower pore diameter) and there will naturally be an increasing percentage of the total cumulative pore volume represented by pores of radius less than the arbitrary pore diameter. Therefore, there is very little point in presenting the data in this way, especially as the pore size distribution data give pore size values incorrectly displaced by one or two orders of magnitude towards finer pore sizes. However, it should be emphasised that the threshold diameter data do give a very good indication of pore refinement in this system.

In mortars and concretes, a small but significant proportion of the total intrusion takes place at pressures lower than the threshold pressure. This, as Diamond points out, is probably due to microcracks and bleeding channels associated with the aggregate–paste interface and the restraint of the aggregate to paste shrinkage. Thus, the threshold effect is less sharply defined. Thus, it may be appropriate to restrict measurements of threshold diameter to paste only rather than mortar and particularly concrete.

Diamond states that the mercury intrusion technique should in addition provide useful information on total intruded (open) pore volume. This however should also be qualified in that the drying method employed for the paste will influence the pore volume recorded. The volume stability and chemical stability of the cement hydrate phases are very sensitive to relative humidity. For example, ettringite has been shown by Glasser [5] to transform under particular drying régimes, and the moisture content of C–S–H gel (and hence its specific volume) is sensitive to temperature and relative humidity. In addition, rapid drying at high temperatures (typically 105 °C) could introduce severe moisture gradients leading to degradation of hydrate phases and to stress concentration and microcracking. Therefore, the drying method should be gentle and should slowly bring the specimen to equilibrium with its drying environment. Zhang and Glasser recommend D-drying for calcium aluminate cements and probably also Portland cements in order to prevent degradation of AFt and AFm phases, and they indicate that desiccant drying using silica gel is also effective. O'Farrell et al. [6] recommend drying to constant weight at 40 °C over silica gel in a closed environment.

References

[1] S. Diamond, Mercury porosimetry — an inappropriate method for measurement of pore size distributions in cement-based materials, Cem. Concr. Res. 30 (2000) 1517–1525.

[2] N. Hearn, F. Young, W/C ratio, porosity and sulphate attack—a review, in: J.P. Skalny (Ed.), Materials Science of Concrete: Sulphate Attack Mechanisms, The American Ceramic Society, Westerville, OH, 1999, pp. 189–205 (Special Volume; ISBN 1 57498 074 2).

[3] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, Cem. Concr. Res. 29 (1999) 933–943.

[4] J.M. Khatib, S. Wild, Pore size distribution of metakaolin paste, Cem. Concr. Res. 26 (10) (1996) 1545–1553.

[5] L. Zhang, F.P. Glasser, Critical examination of drying damage to cement pastes, Adv. Cem. Res. 12 (2) (2000) 79–88.

[6] M. O'Farrell, S. Wild, B.B. Sabir, Pore size distribution and compressive strength of waste clay brick mortar, Cem. Concr. Compos. 23 (2001) 81–91.