Pergamon

Cement and Concrete Research 31 (2001) 1655–1656

CEMENT AND CONCRETE RESEARCH

Discussion

Reply to the discussion by S. Wild of the paper "Mercury porosimetry—an inappropriate method for the measurement of pore size distributions in cement-based materials"☆

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Received 11 July 2001

I thank Dr. Wild for his interesting discussion. It appears that we are in agreement in terms of the inherent unsuitability of MIP as a method for quantitatively determining pore size distributions in hydrated cements. Once this is accepted, it naturally follows that dividing up the MIP size distribution into arbitrary ranges of apparent pore diameter has little point, as Dr. Wild indicates.

Nevertheless, it is evident that MIP can indeed provide some indication of "pore refinement" with age or with increasing content of a fine mineral component, as was demonstrated by Khatib and Wild [1] for metakolinite-bearing pastes. The progressive reduction in both threshold diameter and total intruded porosity can reasonably be used as qualitative indicators of changing pore structure.

The degree to which the total volume of mercury intruded can be used as a reliable indicator of porosity in a specimen is a complicated question. To begin with, the measurement is arbitrary in that the pressure, hence intrusion, is limited by the capacity of the pressuring device. The pressuring capacity of current commercial instrumentation is limited to about 430 MPa (60,000 psi); pressures much beyond this result in solidification of the mercury. Accordingly, an unknown population of fine but open pores cannot be intruded in MIP. There may also be an unknown but not trivial content of pores of larger sizes that are protected from intrusion by being entirely surrounded by solid hydration products.

The influence of specimen preparation on the total pore space measured by MIP, alluded to by Dr. Wild, is an additional complication. Obviously, water needs to be removed from a given space before mercury can intrude. The effect of drying on the internal crystal structure of ettringite or monosulfate (as elegantly elucidated by Zhang and Glasser [2]) is beside the point. With respect to the MIP tally of pore space, what matters is not the change or loss of crystal structure on heating, but the extent of any new intrudable space created by the drying process. Since most cement pastes have very modest contents of ettringite, usually only a few percent, and little monosulfate, the potentially intrudable space created by dehydrating these substances is accordingly minor. With respect to microcracking induced by oven drying, in the writer's experience with backscatter SEM of oven-dried specimens, only occasional microcracks are found and their volume relative to that of the total pore volume is negligible.

In any event, these potential artifacts of rigorous drying need to be balanced against the possibility of incomplete removal of water if the less rigorous drying methods proposed by Wild are used. Incomplete removal of water from dense regions in the paste ("choke points" for mercury intrusion) may occur in D-drying. It would certainly occur in even more incomplete water removal accomplished by "gentle drying to constant weight at 40 °C over silica gel in a closed environment" method mentioned by Wild. Accordingly, in specimens dried by these more gentle methods, mercury likely will not penetrate some areas guarded by incompletely dried entryways, leading to an underestimate of open porosity. This effect is opposite to the possible overestimate in intrudable porosity induced by oven drying.

In my view, the result of these partly offsetting uncertainties is that, whatever drying technique is used, the measured intruded volume is only a rough approximation to the actual pore volume of the paste. For the purpose of comparing *changes* in pore volume with age, or with increasing content of a fine mineral component, any reasonable drying technique can probably be used, as long as it is consistently applied across the series compared.

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

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PII: S0008-8846(01)00617-2

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