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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☆

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1. Introduction

I fully agree with Prof. Diamond's conclusion that mercury porosimetry is an inappropriate method to be used on cement-based materials. Diamond showed that the Washburn equation could not be applied to study pore characteristics of cement-based materials. I would like to go a little further than that. Mercury porosimetry has been used, in the cement field, both to measure the total pore volume and pore size distribution. In the following I shall endeavour to show that the measured characteristics (both total pore volume and pore size distribution) of a specimen have no relevance to that of a companion untreated specimen.

2. Uncertainty in pore volume measurement

In the usual procedure of sample preparation, a small specimen is first dried to remove all traces of existing fluid; for example, Cook and Hover dried their specimens to D-dried state [1]. The dried specimen is then placed in the test chamber, evacuated, mercury introduced and pressure applied. It is known that a cement paste undergoes an irreversible shrinkage during the first drying. The extent of this irreversible shrinkage increases with the severity of drying. It is obvious that the irreversible volume reduction of the first drying is not measured at all by mercury porosimetry. This means that the pore volume measured in mercury porosimetry is definitely less than that of a companion but virgin specimen. Irreversible drying shrinkage shows that the pore structure of the specimen has been altered during the first drying. It has been reported that first drying causes crack formation even in less than 1 mm thick cement pastes specimens [2,3]. The width of some of the cracks is such that mercury enters them under the pressure necessary to keep the specimen submerged in it. This is another factor adding to the uncertainty in pore volume measurement. In his paper Diamond has noted this type of mercury intrusion in specimens subjected to less than threshold pressure. Thus the total pore volume measured in a specimen is less than that of a companion, virgin specimen by an unknown and apparently unknowable fraction.

3. Uncertainty about the relevance of measured pore size distribution

Diamond has enumerated a number of uncertainties in the measurement of pore size distribution. Even if those uncertainties could be overcome, the measured size distribution could not have any relation to that in an untreated specimen. A phenomenological analysis of the normal drying process shows that each volume of the drying cement paste specimen is subjected first to a compressive stress and then to a tensile stress (cf. Ref. [4]). During the compression stage the solid particles are brought nearer to each other than their original separations. The drying shrinkage and the irreversible drying shrinkage are the part manifestations of this rearrangement. During the tension stage the solid particles are separated from each other. This separation starts from the compressed state of the solid particle assembly. Formation of drying cracks shows that this separation does not occur evenly over the whole volume of the specimen. At the cracks the separation is wider than other places. The net result of the drying process is an extensive alteration of the original pore structure; some original pores have been made narrow and others have been made wide. The extent of this alteration depends on the size

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of the specimen, the rate and extent of drying. At present there is no way to evaluate the extent of these alterations. These are the unavoidable consequences of normal drying of cement-based materials. Only the critical point drying may avoid these alterations. In mercury porosimetry, mercury intrudes the altered specimen and reflects its altered characteristics and not those of unaltered specimen. This also means that the results of mercury porosimetry could not be related to many of the physical and chemical characteristics of virgin specimen.

4. Other considerations

Structure alterations during drying have other and more important implications. Many researchers, especially Powers, Feldman and Sereda, and Wittmann, have used water vapour absorption technique to infer important characteristics of set cement pastes. For example, Powers used the water absorption technique to infer and estimate the volume of gel porosity. In all water vapour measurement experiments the paste specimens have to be dried near to zero percent relative humidity. One may wonder to what extent those results have been affected by the altered structure of the dried specimens.

References

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