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Discussion

Reply to the discussion by S. Diamond of the paper "Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry: a comparative study between oven-, vacuum- and freeze-drying"☆

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I would like to thank Dr. S. Diamond for his interest and valuable contribution. He has pointed out many key aspects concerning the applicability of mercury intrusion porosimetry (MIP) to cement-based materials.

First of all, I would like to underline that the main purpose of the presented work was to recall and to show that for laboratory teams using the MIP as a routine technique, much attention has to be paid to the material preparation. The second one was to suggest a less damaging method to dry the specimens.

Fundamentally, one cannot disagree with most of the points raised by Dr. S. Diamond concerning the inappropriate use of the MIP to obtain the pore size distributions of cementitious materials [1].

Undoubtedly, the Washburn–Laplace pore distribution model is not adapted to cements. Pores are effectively not cylindrical and porous space is not an ideal percolative network. Accessibility is another major aspect. The intrusion of internal larger pores and the segmentation of capillary pores by the gel ("choke points") are also of much concern. It is true that the occurrence of "ink bottle" pores is responsible for the overestimation of fine pores and for the underestimation of larger capillary pores. As shown in Ref. [1] by Dr. S. Diamond, backscatter SEM image analysis allows reaching the shape and degree of convolution of the pores. This method allowed detection of pores related to air voids—between ten and several hundred micrometers—in cement pastes while the MIP pore size distributions did not reveal such a porosity. However, it should be mentioned that for aged pastes with w/c around 0.40 (well prepared), the occurrence of such pores remains relatively low. The SEM technique is extremely valuable to observe in two dimensions the microstructure of hydrated cements, but direct three-dimensional observation is still very difficult [2]. Actual resolution level is also limited, globally around 1 μm, and thus the nanoporosity cannot be explored. It should be also considered that sample preparation may introduce microstructure disturbances.

Talking about the problem of water removal, I agree with Dr. S. Diamond when he suggests that incomplete drying leaves water plugs in the smallest pores and thus limits the intrusion of mercury. Therefore, it is clear that many reasons make MIP an imperfect method for cement paste pore-structure analysis. Nevertheless, as mentioned by Wild [3], "most people using the technique for this purpose already knew or at least suspected" the MIP limitations. Now, should we stop to use this technique? I do not think so! At present, given that other techniques such as SEM image analysis, X-ray microtomography and associated digital image processing methods still need to be improved and cannot be easily implemented, MIP is still an acceptable tool to comparatively study the pore-structure evolution of cement-based materials in various environments (Fig. 1). Compared to other methods (adsorption, thermoporometry), it is one of the methods that effectively provide microstructural information—pore size distribution—for a large pore range. Finally, MIP can provide critical knowledge on the relationships between microstructure and transport properties.

Another topic was raised by Dr. S. Diamond concerning the results about the impact of the drying procedure. Dr. S. Diamond suggested that the "results confirm the great impact of the drying on the MIP results, rather than on the actual pore structure." I think that although the pore size distribution estimated through MIP is not the exact reflection of the real

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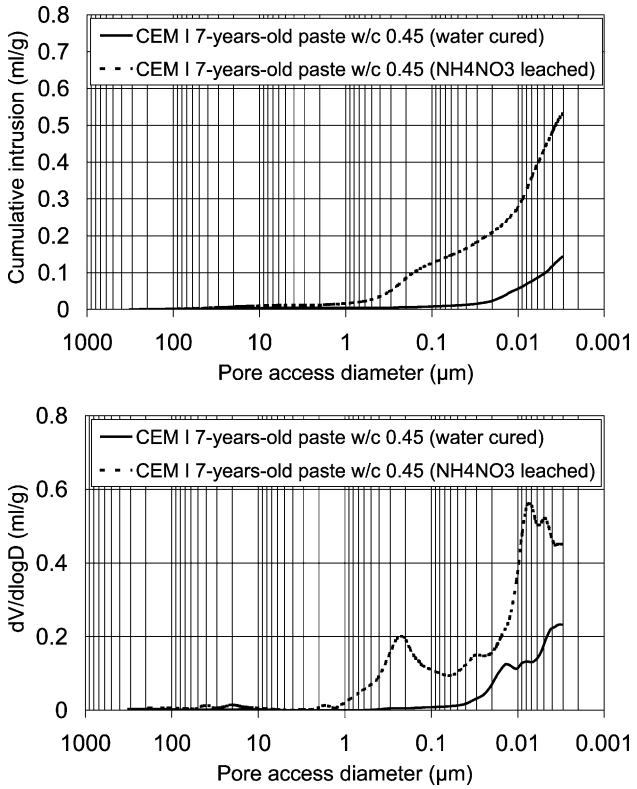

Fig. 1. Examples of CEM I paste MIP pore size distributions, cumulative and differential, obtained in various contexts.

one, results were significant enough to point out the influence of the drying technique. Considering that cement hydrates are in equilibrium—volume and chemical stability—with the relative humidity, I believe that moisture gradients and desiccation stress generated by oven drying is much more harmful than pore-structure alteration due to freeze-drying. The effect of oven drying is probably worse with concretes. In that case, differential thermo-hydromechanical behaviour of the paste and of the aggregates is responsible for important damages [4]. Chatterji [5] recalled that during the drying of cement paste there is irreversible shrinkage that may generate microcracks, introducing new uncertainties in the pore-volume estimation. But in my opinion, the impact is more quantitative (pore structure) than quantitative (total porosity).

As a conclusion, I would say that when using MIP, we have to keep in mind all the limitations of this technique. Other ‘‘routine’’ techniques are needed to investigate the pore structure of cement-based materials at nanoscale and to complete the MIP, which may not be so successful but is still widely used.

References

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