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Discussion

A discussion of the paper "Effect of drying on cement-based materials pore structure as identified by mercury porosimetry—a comparative study between oven-, vacuum-, and freeze-drying" by C. Gallé☆

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Dr. Gallé has presented a well-written and detailed study of the effect of extent of drying of cement pastes and concretes on MIP results. Unfortunately, I believe that his interpretations, while conventional, are in fact fundamentally misleading. The reasons are as detailed below.

To begin with, in his Introduction, Dr. Gallé cited my recent paper [1] as one of a list of 14 citations described as showing that "Mercury Intrusion Porosimetry (MIP) has been successfully used for a long time." In point of fact, my paper drew exactly the opposite conclusion. As indicated by its title, the paper presented evidence that MIP is an *inappropriate*, rather than a successful, method for determining the pore structure of cement systems.

The fundamental problem lies with the MIP experiment itself. In MIP, specimens are first evacuated and then intruded by mercury under successively increased pressures. The resulting intrusion vs. pressure data are then conventionally converted to pore volume vs. pore diameter (or radius), using the well-known Washburn equation. The necessary assumption is made that larger pores can be intruded from the outside without the mercury having to penetrate through smaller pores. Evidence was presented in Ref. [1] that this is not so; instead, large regions of cement paste are not intruded by mercury until pressures are reached that are high enough for the mercury to penetrate extremely narrow entryways. Thus, large pores in the interior of the specimen are not intruded until high pressures are reached, and their volume is necessarily interpreted as belonging to much finer pores.

These effects have long been of concern, and were mentioned by the present writer and his colleague more than 30 years ago [2]. However, it was not until backscatter mode scanning electron microscopy permitted direct observations of pore sizes in cement paste that the enormous magnitude of this effect became apparent. As carefully detailed in a previous study [3], multimicron-sized capillary pores and even air voids of several hundred microns in actual diameter are tallied by MIP as pore spaces of diameters less than 0.1 μm.

These narrow entryways are not single narrow pores, nor are they individual 'ink bottle' pores. Rather, the paths for intrusion of mercury likely contain multiple choke points along individual flow paths from the pressurized mercury reservoir to the center of the specimen. The concept is not new. As summarized by Neville [4], capillary pores "form an interconnected system randomly distributed throughout the cement paste," and "in mature and dense pastes, the capillaries can become blocked by gel and segmented, so that they turn into capillary pores *interconnected solely by gel pores*." Narrow interconnections or choke points (whether or not they are actually gel pores) permit intrusion by mercury into guarded portions of the specimen only when high pressures are reached, even in rigorously dried specimens. The effect of the nature of this pore system on MIP is that MIP experiment, as conventionally interpreted, does not in fact measure anything like a true pore size distribution.

Gallé's results clearly show this effect. His PSD plots for all of the cement pastes, as shown in his Fig. 4, show that negligible mercury intrusion occurred until pressure was reached equivalent to about 0.1 μm (or smaller, with some specimens)—in other words, that the largest pore diameter tallied was 0.1 μm. Backscatter SEM micrographs published by various authors of cement pastes similar to Gallé's confirm the ubiquitous presence of pores 10 μm or more. A representative micrograph showing the usual content of such multimicron diameter pores was provided as Fig. 2 of the original reference cited [1].

☆ Cem. Concr. Res. 31 (2001) 1467–1477.

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It is slowly coming to the attention of the scientific community that MIP results are not proper representations of the pore systems being analyzed. To his credit, in his MIP plots, Dr. Gallé labels his pore diameter axis as "pore *access* diameter" rather than "pore diameter." Unfortunately, this nomenclature begs the question. Labeling the results as "pore access diameters" might be appropriate if the system contained individual narrow-necked or ink bottle pores that could be individually accessed by mercury. This is not the case.

The main thrust of Dr. Gallé's paper is focused on the specific effects of various less rigorous drying procedures carried out prior to the MIP experiment. Paradoxically, in his introductory statement, Dr. Gallé indicates that "An MIP test demands *complete* water removal from the specimen"; yet his own data testify to the degree that the water removals effected by the less rigorous drying procedures he espouses are, in fact, incomplete.

Wild [5], in his recent discussion of Ref. [1], raised the question of the desirability of gentle but incomplete drying methods, specifically 'd-drying' and 'gentle drying at 40 °C over silica gel.' In reply [6], I suggested that incomplete drying likely leaves plugs or residual water in the narrowest choke points, which may induce complete pore blockage to mercury in some areas of the paste. Other entryways may not be completely blocked, but would be narrowed by 'collars' of sorbed water, thus requiring higher mercury pressure to effect entry. The expected effects of incomplete drying on the MIP would thus be (a) some reduction in the total intruded pore volume, (b) narrowing of the threshold diameters, and (c) MIP intrusion curves generally skewed toward smaller pore diameters compared to those for fully dried specimens of the same material.

Of course, such effects need to be weighed against the opposite effects of possible alteration in the paste pore system that might result from the rigorous drying necessary to completely remove the water. Dr. Gallé expresses the conventional (if vague) concerns about what damage drying might do to the delicate fine structure of the cement paste, concerns that are commonly expressed in the literature but which, as indicated in Ref. [6], may be vastly overdrawn.

It is interesting to examine Gallé's results from these perspectives.

To begin with, Gallé's Figs. 1 and. 2 show the degree to which the progressively less rigorous drying methods leave progressively more water in the paste. Vacuum drying and oven drying to 60 °C each removes about 15% less water than oven drying; Gallé prefers to consider that the water content of the oven-dried pastes is somehow "overestimated" by this amount. The water removal on freeze drying is even more incomplete, with freeze drying leaving additional amounts of water behind.

The effects of drying method on total mercury intrusion seen in Gallé's Fig. 5 are significant for Portland cement pastes, but negligible for slag cement pastes. Substantially less total intrusion is seen for less rigorously dried Portland cement pastes of w/c 0.30 and 0.50, but for some reason, the effect on the w/c 0.40 paste is practically made up by delayed intrusion at very high pressure. On the other hand, in his Fig. 8, the effect of drying method is very pronounced and very obvious. Much less total intrusion is registered for 60 °C dried concrete than for 105 °C dried concrete, and the total intrusion for freeze-dried concrete is still further diminished.

Gallé's interpretation of this effect is very different from that suggested in this discussion. In Dr. Gallé's terms, "these results confirm the great impact of oven drying on the concrete pore structure." Based on the great discrepancy between measured MIP pore size distributions and actual pores observed in backscatter mode SEM, I believe that these results confirm the great impact of method of drying on the *results of the mercury intrusion experiment*, rather than on the actual concrete pore structure.

The expected effect of drying method on threshold diameter is clearly evident in Gallé's Fig. 4. For each of the Portland cement pastes, the threshold diameter exhibited for 105 °C drying is about 0.1 μm; it is reduced progressively for drying treatments that leave behind progressively more water. The expected trend of MIP size distributions progressively skewed to finer apparent pore sizes with progressively less complete dehydration is also apparent.

However, the major point of this discussion is not that the MIP data obtained with progressively less effective removal of water show less complete intrusion and apparently finer pore structure, although these effects are present. Rather, it is that the MIP pore size distributions, however, obtained with whatever drying treatment badly reflect the real sizes of pores in the system and vastly underestimate them. Failure to remove all of the water from the specimens prior to subjecting them to mercury intrusion simply makes the effect worse, making an inappropriate measure of pore size distribution even more inappropriate.

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