Mercury Intrusion Porosimetry

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Introduction

Cement-bonded building materials like concrete and mortar are porous with a complex internal pore system. They can be described as a compound of aggregate particles dispersed in a matrix of cement paste. The hydrated cement paste contains capillary pores with a big variation in size resulting from cement particle spacing in the cement water suspension, and smaller gel pores which are the interlayer in the Calcium-Silicate-Hydrate (C-S-H) or other hydrate products. Additionally, spherical air voids with large diameters of more than twenty microns, naturally or artificially introduced, are present. Furthermore, around the aggregates a porous interfacial transition zone is present. The pore sizes range from a few nanometers up to several microns and the geometry of the pores exhibit rather different and complex shapes. Mercury intrusion can detect a wide range of pore sizes from meso- to macropore sizes (2 nm to 100 µm).

Measurement Principle

Figure 1: Mercury intrusion porosimeter

The determination of pore size following the technique of mercury intrusion is based on the behavior of “non-wetting” liquids in capillary. A liquid coming in contact with a solid porous material and behaving as a non wetting agent (namely if the contact angle of the liquid with that solid material exceeds 90°) cannot be spontaneously absorbed by the pores of the solid itself, because of surface tension. However, this resistance to penetration can be won by applying an external pressure. Required pressure depends on the pore size. The relation between the pore size and the applied pressure, assuming the pore is cylindrical, is expressed as:

$$p = -\frac{2\gamma\cos\Theta}{r}$$

p. absolute applied pressure; r: pore radius
γ: mercury surface tension (≈0.48 N/m); Θ: contact angle (≈ 140°)

This relation is commonly known as Washburn Equation.

Relevance for Our Field

The biggest obstacle for this method is the absence of a unique theory for interpretation of hysteresis phenomena encountered between intrusion and extrusion. Large amounts of entrapped mercury remains in the pore space after the full intrusion/extrusion cycle. Pore network effects significantly influence the results. Larger pores (so-called ink-bottle pores) may be accessible to the mercury through much smaller pores (neck entrances) only. The ink-bottle type pores hence do not get filled with mercury until the applied mercury pressure reaches the level for filling its neck entrances. In this way such pores are systematically underestimated in size.
The pore network of cement-based systems may be described as a network of large chambers interconnected by smaller necks. Air pores and coarser pores at the interfacial transition zone around aggregates also may be of ink-bottle type.

Example

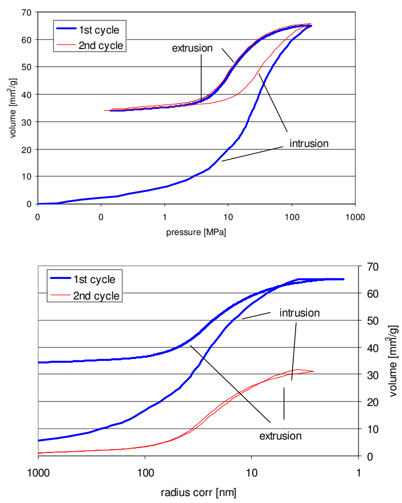

Figure 2: Mercury intrusion and extrusion curves

In cement-based materials it is assumed that after the first cycle all ink-bottle type pores remain mercury filled. This assumption is supported by the observation that no additional mercury remains entrapped in the pore system after completion of the second cycle. Comparing the total porosity derived from the 1st cycle with the one obtained in the 2nd cycle one can conclude that more than about 50% of the pore space is ink-bottle type.
Hence, in a second cycle the purely non ink-bottle type pore space (connected pore space) is analyzed. However, the hysteresis persists. Pore network effects can not be the main cause for such significant hysteresis anymore.
This leads to the assumption that in mercury intrusion experiments the surface tension, contact angle or form factors vary whether the meniscus is advancing receding. This phenomenon is also found for other wetting and non-wetting fluids. Therefore a simple contact angle shift from 140° for intrusion to 107° for extrusion (recending mercury meniscus) was applied. This leads to a correction of the radius by a factor of 2.657 and a very good agreement between intrusion and extrusion data (second cycle) is found.

Applications & Potentials

We may conclude that in a mercury intrusion experiment we can determine

A) the total amount of pores (of a dried pore system).
B) the amount of ink-bottle type pores.
C) the size distribution of the pores that are connected through larger pores to the surface. This calculation can be done when an additional second mercury intrusion cycle is performed.

The size distribution of ink bottle type pores can not be analyzed. However, executing a second mercury cycle it may be possible to evaluate

D) the size of the neck entrances by a subtraction of the second from the first intrusion curve.

J. Kaufmann, R.Loser, A.Leemann, *Analysis of cement-bonded materials by multi-cycle mercury intrusion and nitrogen sorption*, J. Colloid Interface Sci. 336, 730-737 (2009).

J. Kaufmann, *Pore space analysis of cement-based materials by combined Nitrogen sorption - Wood's metal impregnation and multi-cycle Mercury intrusion*, to be published in Cement and Concrete Composites (2010).

Limitations

The data interpretation of Mercury intrusion porosimetry is based on many assumptions on pore geometry and the interpretation of connectivity effects. Even the values for the contact angle and the surface tension can not be considered to be accurate but are rather “good assumptions”. Furthermore, the samples have to be dryed prior to measurement and the degree of drying strongly influences the result. Additionally only relatively small samples can be analyzed, which may not represent a representative volume.

Nevertheless Mercury intrusion porosimetry is a powerful tool for a mostly qualitative analysis of the composition of the mesoporous pore space of cement-based pore systems.