MICROTRAC

PORE SIZE MEASUREMENT OF HARDENED CEMENT PASTE AT VARIOUS MATERIALS MOISTURE CONTENT WITH MERCURY INTRUSION POROSIMETRY

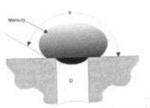
Introduction

Hardened cement paste (HCP) is the glue in concrete and mortar. HCP is a porous, heterogeneous material composed mainly of Calcium Silicate Hydrates (C-S-H). These are of micron to nanometer size, forming pores on a nanometer scale. Thus, HCP can be regarded as a colloidal system where surface forces play a remarkable role. Adsorbed water molecules interact with the surface. Capillary condensation occurs in the pores below bulk conditions, acting in the form of capillary and disjoining forces, the latter can reach into GPa ranges. All these forces can alter the structure and properties of the hardened cement paste depending on the moisture content. Pore size distributions were measured with mercury intrusion porosimetry on hcp specimens, which had been prestored over the entire range of relative humidity. Swelling and shrinkage of HCP tubes were also determined. The pore size distribution is corrected for each humidity step regarding the particular porosity, contact angle, and volume change. The pore size distribution as a function of relative humidity is nonlinear and characterized by an extreme value in the medium range of humidity.
When evaluating the compressive strength of a hardened cement paste consisting of Portland cement (CEM I, w/c=0.4, calcium hydroxide storage for at least 28 days), a minimum strength is documented at a medium relative humidity level [1]. Not only the above-mentioned mechanical properties but also the physico-chemical characteristics are influenced [2]. For instance, both the specific surface determined by measurements of small-angle neutron scattering (SANS) [3], as well as by Beddoe et al, who measured small-angle X-ray scattering (SAXS) [4],

Basics of Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry is described in the ISO standard ISO 15901-1. The non-wetting mercury is forced into accessible pores at ambient temperature with pressures up to 414 MPa, entering pores down to ca. 3.6 nm pore diameter (***Figure 1***). The pore volume corresponds to the amount of mercury intruded. According to the Washburn equation, the pore size (radius, diameter) is inversely proportional to the applied pressure.

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



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With pore radius *r* [m], surface tension of mercury *g*= 0.48 N/m, and intrusion pressure *p* [Pa].
With a contact angle *q* =141.3°, a simple estimation for the pore radius is obtained $r \approx 0.7500/p$.

BELPORE - the Device for Safe Mercury Intrusion Porosimetry

The BELPORE mercury porosimeters can measure pore diameters from 3.6 nanometers up to 1 millimeter. They consist of 3 models: **BELPORE LP** as a mercury filling device and for low pressures, **BELPORE MP** for medium-high pressures and **BELPORE HP** for high pressures, details see Figure 1.
The BELPORE mercury porosimeters work according to the P.A.S.C.A.L. principle, which is not only a pressure unit. In the BELPORE porosimeter, it means the equilibrium-controlled and optimized control of the pressure build-up by "Pressurization by Automatic Speed-up and Continuous Adjustment Logic". This automatic control is driven by the real pore system and allows shorter measuring times with guaranteed equilibrium conditions and detection of all pores within the specification, up to 20,000 measuring points per analysis. Pressure tables are thus superfluous. Since only two types of dilatometers (sample cells for powder or solids) are sufficient for most measuring tasks, and no gases or liquid nitrogen are required, running costs can be kept significantly lower. Other innovations include simplified operation of the BELPORE LP low-pressure porosimeter and employing the ultra-macropore dilatometer an extended measuring range up to pore sizes of 1 millimeter, applicable for thin membranes. Vertical degassing and filling with mercury on the BELPORE LP is not only fast but also allows the degassing pressure to be adjusted. Therefore, it is possible to measure moist samples without changing the material's moisture. The 3-D evaluation software PoreXpert is optionally available. With this software, e.g., tortuousness, diffusion, percolation, and much more can be derived from porosimetry data.

The correction of pressure-induced materials compression is incorporated, from which the bulk modulus value is calculated. BELPORE porosimeters are available in pressure ranges from 0.01 kPa to 450 kPa (and mercury filling), 0.1MPa to 228 MPa, or up to 414MPa (***Figure 1***). High precision measurements are finished in less than 1 hour, and for quality control, it can go down to 9 minutes.

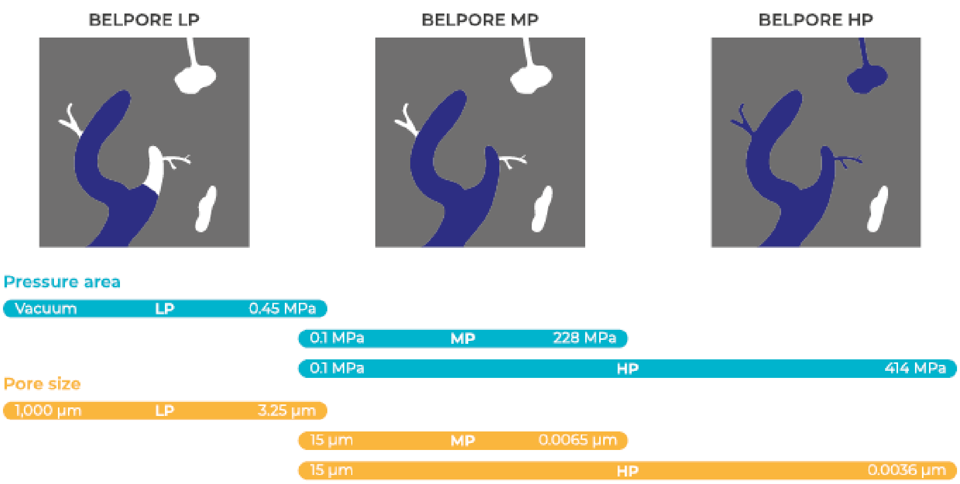

Figure 1. Pressure ranges and accessible pore sizes of the BELPORE porosimeters

Results

In [5], experiments were conducted on hardened cement paste made from Portland cement with water/ cement ration w/c=0.4. After 28 days of curing in saturated Calcium Hydroxide solution, these samples were stored at various relative humidities over saturated salt solutions. The contact angle of mercury with the cement paste surface in Washburn's equation becomes a function of the relative humidity instead of the usual constants (e.g., 140°). The contact angle shows a minimum at medium humidity levels [5]. At this medium humidity, the porosimeter measurements reveal a pore size maximum in the pore range from 10 to 50 nm, with the humidity-dependent contact angle representing only a marginal correction, which means that a genuine, significant structural change in the porous material occurs. These findings are also recognized in ISO 15901-1 regarding the materials' moisture content, e.g., for hydrates in sample preparation for mercury porosimetry. The latest BELPORE porosimeters enable measurements without any interference with the moisture content of the cement paste samples due to the vertical mercury filling of the dilatometers (sample cells) at a defined degassing pressure (***Figure 2***) above the water vapor saturation pressure, same as described in [5] with a predecessor device. This result of moisture-dependent pore size changes is supported by the non-invasive, high-resolution measurement of small-angle X-ray scattering (SAXS) [7]. It thus appears likely that these humidity-related changes in the pore size also influence the diffusion characteristics, and thus on possible chemical reactions such as carbonation. An example of the humidity on pore size changes is shown in ***Figure 3***. The references listed below contain details regarding the above-described tests and analyses as presented in ***Figure 4***.

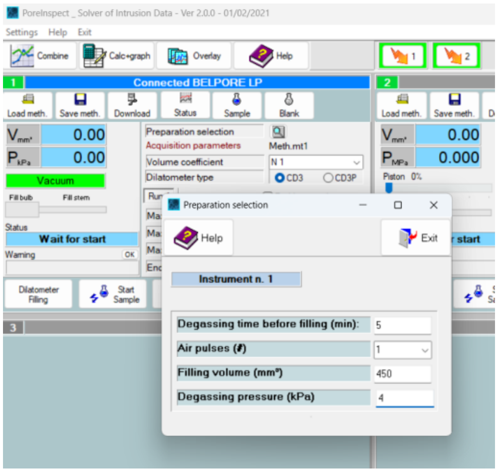

Figure 2: Setting of degassing pressure 4 kPa, which is above water vapor saturation pressure, therefore avoiding any material's moisture changes.

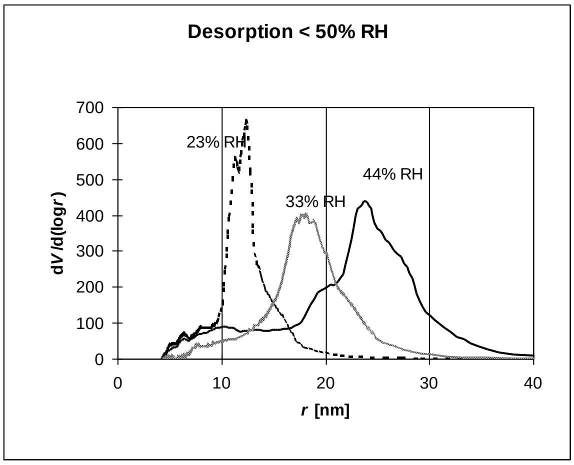

Figure 3: Example of humidity-dependent pore size shifts in hardened cement paste, calculated with humidity-dependent contact angle

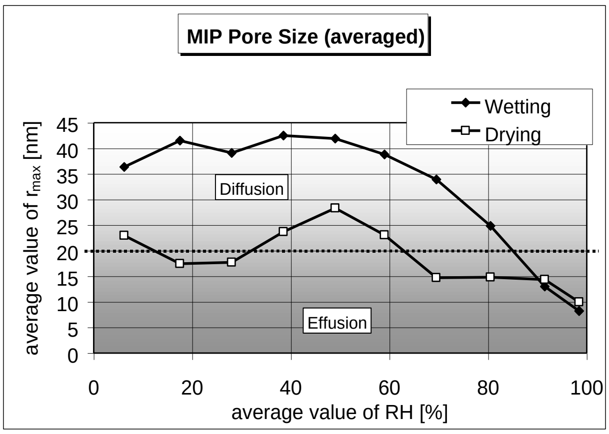

Figure 4: Summary of pore size shifts of prestored hcp at various relative humidities.

Conclusion

In conclusion, only a better understanding of the interactions between humidity and the hardened cement paste as a nanoporous, colloidal hydrate system will ultimately lead to a significantly greater durability of concrete structures in construction practice. Moreover, a more reliable, broadened knowledge of the interactions between water and cement paste on the micro and nano levels is of crucial importance for modeling, simulation, and life cycle forecasts.

BELPORE analysis of hardened cement paste at various moistures stands for:

- Mercury Intrusion Porosimetry according to ISO 15901-1
- Fast and accurate measurements of pore size and volume, even on moist materials
- Safe and easy handling
- Small lab space
- Advanced results for cement-based materials under real-life conditions

References

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For more information about the **BELPORE Series**: [Mercury Porosimeter BELPORE - Microtrac.com]