Laboratory of Construction Materials

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Mercury Intrusion Porosimetry (MIP)

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The technique explained

Many solids and powders contain a certain internal volume of empty space. This space is distributed within the solid as pores, cavities and cracks. The sum of all these void volumes is called porosity.

There are basically two types of pores: closed pores and open pores. Closed pores are isolated from the external surface, not allowing the ingress of external fluids. They influence parameters such as density, along with properties such as strength and thermal properties. Open pores are connected to the external surface and are accessible to fluids.

The principle of MIP is based on the fact that mercury behaves as a non-wetting liquid towards most substances. Mercury is forced to enter into the open pores by applying a controlled increasing pressure. The volume of mercury intruded in the sample is detected using a capacitive system.

We can then relate the pressure applied to intrude a differential volume of mercury with the size of the pore using the Washburn equation:

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

P : pressure
γ : surface tension
θ : contact angle
r : capillary radius

Material	Contact Angle
Cement paste	120º - 140º
Mica	126º
Clay	139º - 147º
Calcite	146º
Quartz	132º - 147º

Reference values mercury contact angle with different sample surfaces.

What can we get and limitations

MIP results are in general plotted as cumulative pore volume versus pore entry radius and normalized per sample volume or per gram of material. Three relevant parameters characterizing the pore structure can be determined from classic cumulative MIP curves: total percolated pore volume, threshold pore entry radius and critical pore entry radius.

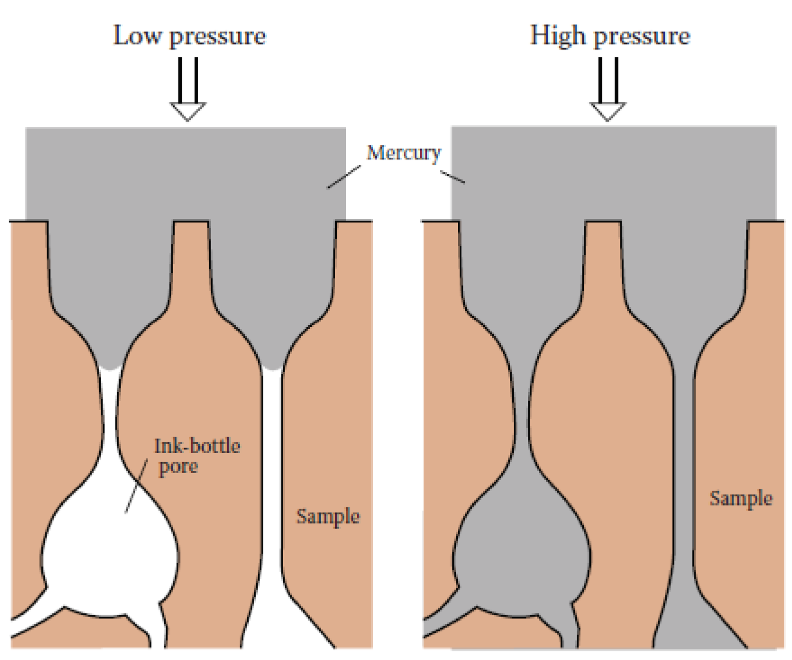
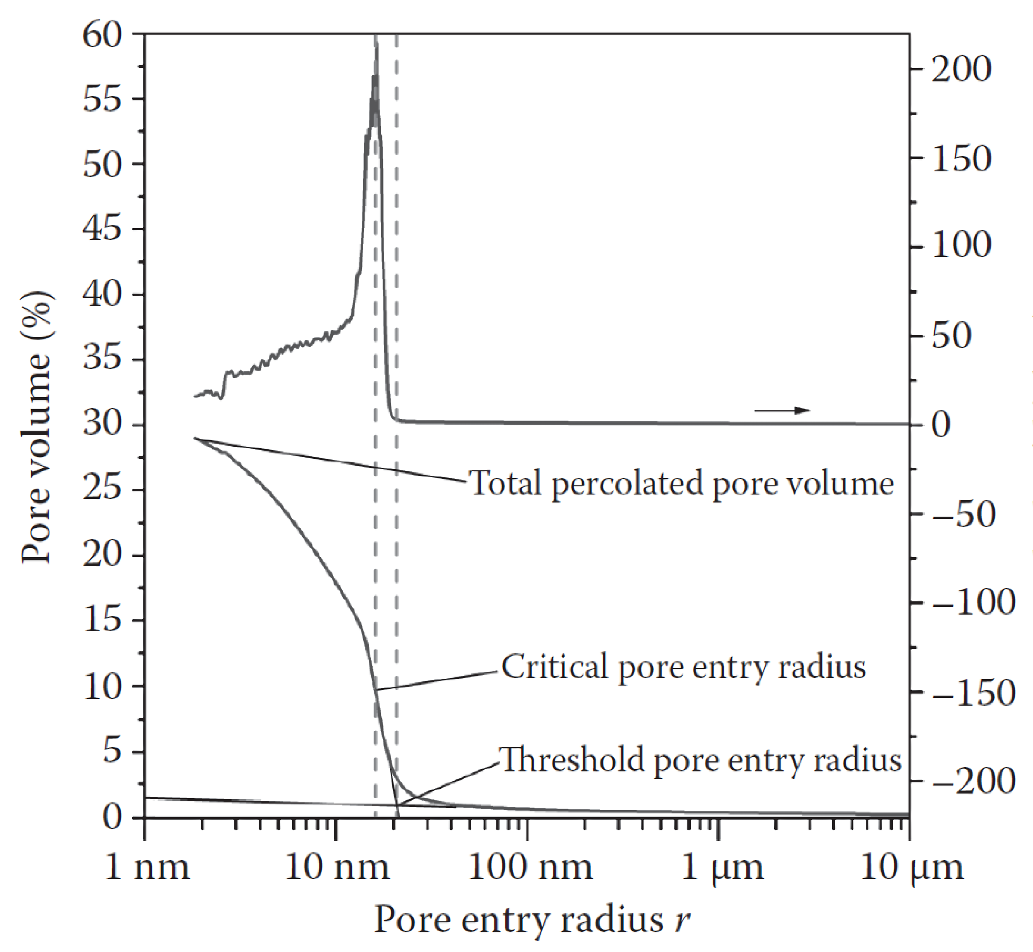


Illustration of ink-bottle pores showing large pore volume only accessible through narrow necks.

The ease of use of the MIP technique and seemingly straightforward interpretation of MIP results often make users forget the assumptions made and the limitations of the MIP technique itself. The large discrepancy of MIP results has sparked fervent discussions on the reliability of the MIP technique. The first key point to keep in mind when doing MIP experiments is that MIP measures the pore entry sizes and not the pore real sizes of the sample. This effect is more significant than it might be expected as often a high volume of pores becomes accessible through increasingly smaller pore entries. This effect is often called the ‘ink-bottle effect’.



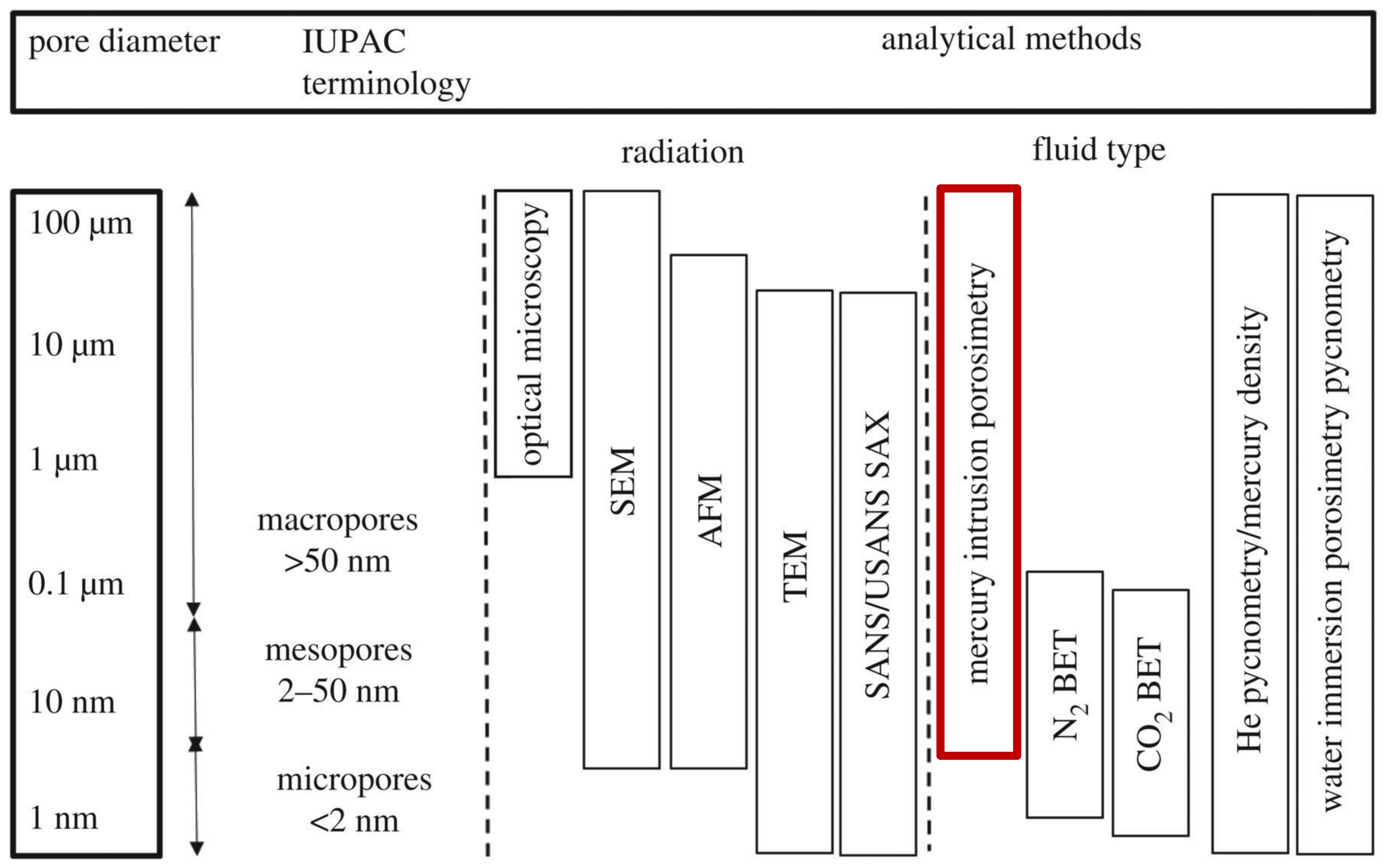
Example of typical MIP cumulative and derivative curves obtained when measuring Portland cement pastes with a maximum MIP pressure of 400 MPa.

Applications to cement science

The MIP technique was for the first time used with cementitious materials in the 1970, means 30 years after the technique was first developed.

Porosity strongly determines important physical properties of the cementitious materials, such as durability, mechanical strength, permeability, adsorption properties etc. The knowledge of pore structure is an important step in characterizing the materials, in order to predict their behaviour under different environmental conditions. The largest pores that can be detected by MIP are up to 1 mm. The smallest measurable pores depend on the maximal pressure applied on the mercury. Today, pores with 2 nm radius can be measured, while in the 1970s the smallest pores were about 12 nm.

The wide popularity of MIP stems from being relatively fast and simple. However, careful sample preparation and data analysis are essential.



MIP among different methods to determine porosity and pore size distribution.

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Anovitz L., Cole D., *Characterization and analysis of porosity and pore structures*, Reviews in Mineralogy and Geochemistry, 80(1):61-164, 2015.