

Mercury Intrusion Porosimetry

Hints on Porosity

Many solid and powder materials, both natural (stones, soils, minerals, etc.) and manufactured (catalysts, cements, pharmaceuticals, metal oxides, ceramics, carbons, zeolites, etc.), contain a certain internal volume of empty space. This is distributed within the solid mass in the form of pores, cavities, and cracks of various shapes and sizes. The total sum of these void volumes is called porosity. Porosity strongly determines important physical properties of materials, such as durability, mechanical strength, permeability, adsorption properties, etc. The knowledge of pore structure is an important step in characterizing materials, in order to predict their behavior under different environmental conditions. There are two main and important typologies of pores: closed pores and open pores. Closed pores are completely isolated from the external surface, not allowing the access of external fluids in neither liquid nor gaseous phase. They influence parameters like density, along with mechanical and thermal properties. Open pores are connected to the external surface and are, therefore, accessible to fluids, depending on the pore nature/size and the nature of the fluid. Open pores can be further divided into dead-end or interconnected pores. Further classification in relation to the pore shape should be determined whenever possible.

In 1842, Smetana first mentioned the possibility to force mercury into wood to prove its porous structure. In 1921, Washburn described how one could obtain a pore size distribution from pressure-volume data for mercury penetration into a porous body. Independently, Loisy made the same suggestion in 1941, and the first ones to apply the technique were Henderson et al. in 1940. Finally, the first paper related to real equipment was published by Ritter and Drake in 1945. In 1970, Rootare gave a comprehensive review of the early developments.

Classification of pores according to their width:

Micropores: Less than 2 nm

Mesopores: Between 2 nm and 50 nm

Macropores: Larger than 50 nm

Specific Pore Volume and Porosity

Internal void space in a porous material generally expressed as a void volume (in cc or ml) referred to the mass unit (g). The porosity is the ratio of the total pore volume to the apparent volume of the solid or powder (excluding inter particle voids).

Pore Size Distribution

Generally represented as the relative abundance of the pore volume (as a percentage or a derivative) as a function of the pore size.

Density

True density: Density of the material excluding pores and inter-particle voids

Apparent density: Density of the material including closed and inaccessible pores

Bulk density (or envelope density): Density of the material including pores and inter-particle voids. Density is expressed as a mass over a volume.

Specific Surface Area

The surface area of a solid material is the total surface of the sample that is in contact with the external environment. It is expressed as square meters per gram of dry sample. This parameter is strongly related to the pore size and the pore volume (The larger the pore volume, the larger is the surface; The smaller the pore size, the higher the surface.) The surface area results from the contribution of the internal surface of the pores plus the external surface of the solid or the particles (in case of powders). Whenever a reasonable porosity is present, the contribution of the external surface to the total is very limited.



Experimental data collected by Pascal 140-240-440 mercury porosimeters by Thermo Electron Corporation, Milan, Italy

Theoretical Aspects

The principle of the technique is based on the fact that mercury behaves as a non-wetting liquid toward most substances. This technique is not advisable when the sample contains metals reacting with mercury (i.e. gold, aluminum, etc.) and forming amalgam. Mercury is forced to enter into the pores by applying a controlled increasing pressure. As the sample holder is filled with mercury under vacuum conditions (mercury surrounds the sample without entering the pores due to the very low residual pressure) during the experiment, the pressure is increased, and the volume of mercury penetrated is detected by means of a capacitive system.

The decreasing volume of mercury in the sample holder represents the pore volume. The method is based on the capillary depressurization phenomenon. In a porous body, the surface tension forces are opposed to the penetration by liquids showing a contact angle higher than 90° (non-wetting liquids). It is necessary to apply a pressure to mercury compensating the pressure difference over the mercury meniscus in the porous body:

$$P = -\Delta P_c = \gamma \left(\frac{1}{r_m} + \frac{1}{r_c} \right)$$

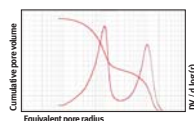
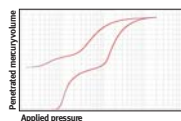
In which ΔP_c is the capillary pressure, γ is the surface tension of mercury, and r_m and r_c are the principal meniscus curvature radii. These last values are in principle unknown in real porous media, therefore, it is generally considered the curvature of meniscus C: $P = \gamma C$. For mercury, it is generally quoted a surface tension of 480 dyne/cm, although for very strongly curved surfaces, the surface tension is also a function of the curvature. The curvature C depends on the contact angle between mercury and the solid and on the pore geometry. For cylindrical capillaries:

$$C = \frac{2 \cos \theta}{r}$$

Where θ is the contact angle, and r is the capillary radius, the combination of the two previous equations leads to the well known Washburn equation:

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

Although in almost any porous media there are no cylindrical pores, the Washburn equation is universally used to calculate pore size distribution from mercury porosimetry data. Most frequent contact angles of mercury are between 130° and 150°, even though larger values have been reported. If θ is unknown, it is generally used an average value of 140°.



CONTACT ANGLE = 141.3°	PRESSURE RANGE (MPa)	PORE SIZE (RADIUS/ nm)	PARTICLE SIZE (DIAMETER/ μ)
Pascal 140	0.013 – 0.4	58,000 – 1,900	330 – 15
Pascal 140 + ultramacropore	0.0013 – 0.4	300,000 – 1,900	3,000 – 15
Pascal 240	0.1 – 200	7,500 – 3.7	40 – 0.015
Pascal 440	0.1 – 400	7,500 – 1.8	40 – 0.01

Hg surface tension = 480 dyne/cm
Kp factor = 4.65

TYPE OF MATERIAL	CONTACT ANGLE
Cement	125
Mica	126
Aluminum Oxide	127
Oxidized Surfaces	140
Zinc Oxide	141
Coal	124
Calcite	146
Paraffin Wax	149
Borosilicate Glass	153
Quartz	132 - 147
Glass	135 - 140
Clay	139 - 147
Titanium Dioxide	141 - 160

Literature

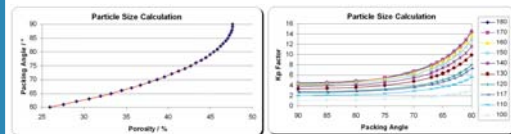
- S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 2nd Ed. (1982)
- E.W. Washburn, Phys. Rev. 17 (1921) 273
- H.L. Ritter and L.C. Drake, IEC Anal. Ed. 17 (1945) 782-787
- R.P. Mayer and R.A. Stowe, J. Colloid Interface Sci., 20,893(1965)

Particle Size Determination

Mercury porosimetry spectra provide information about pores between particles (inter-particle porosity). This behavior was studied by Mayer and Stowe in detail. They supposed that a certain "breakthrough" pressure is required to force mercury penetrating into void spaces between a packed spheres bed. The product of the breakthrough pressure, P_b , multiplied by the surface tension is inversely proportional to the spheres diameter D according to the following equation (Mayer-Stowe model):

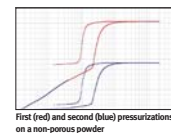
$$P_b = \frac{K_p \gamma}{D}$$

K_p is a dimensionless proportionality factor deriving from a complex function of the contact angle and the packing arrangement of the particles. The packing angle can be calculated by the inter-particle porosity, knowing the real and bulk densities of the material (see tables below). The Mayer-Stowe theory was confirmed experimentally by comparison with other independent techniques (sedimentation and electron microscopy). Best agreement was found for mono-modal particle size powders. Porous powders can be conveniently analyzed by mercury porosimetry. Usually, powders are formed by particles that are interconnected by light-bonding generating agglomerates.

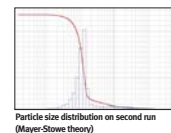


Agglomerates appear to have a larger size than the particle themselves. Mercury porosimetry, being a dry technique under pressure, can break the agglomerates performing a first pressurization run.

Returning to the starting pressure, agglomerates cannot form again, and a second pressurization run measures the inter-particle porosity. If the particles are porous, mercury porosimetry analysis shows two penetration regions: the low-pressure penetration is relevant to the inter particle porosity, while the high-pressure penetration is relevant to pores.



First (red) and second (blue) pressurizations on a non-porous powder



Particle size distribution on second run (Mayer-Stowe theory)

The Importance of "Blank" Curve Correction

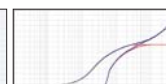
Mercury porosimetry technique involves very high pressure generation, up to 400 mPa. Despite being a liquid, at such high pressure mercury is submitted to a certain compression degree. Additionally, the glass of the sample holder, the dielectric oil, and other parts under high pressure change their properties. The sum of all these side effects generates the so-called "blank curve" that is similar to a penetration curve. Therefore, the blank must be measured with a complete analysis without the sample and then subtracted from the penetration curve. The resulting corrected spectrum now represents the real sample porosity. In case the blank is not properly measured and subtracted, the mercury porosimetry results can lead to big mistakes in pore volume and surface area determination, especially in the case of narrow pores with a small pore volume.

Factors Generating a "Blank" Curve

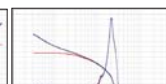
- Maximum pressure reached during the analysis
- Pressurization speed
- Mercury temperature at analysis start
- Mercury volume and sample density
- Dielectric oil type and age
- Temperature effect during pressurization



Typical blank compression up to 400 mPa (about 35 mm³ of mercury compressed)



A penetration plot without (blue) and with (red) blank correction



The pore size distribution showing very small "ghost pores" (blue)

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