PYCNOMETER DENSITY AND POROSIMETRY

Types of densities

Generally, it is possible to define density as a ratio of the powder weight and volume. The weight of the powder can be determined directly by weighing. Determination of the powder volume is more challenging, usually due to irregular shape of particles and including/not including of interparticular and intraparticular spaces that are filled with air. Therefore, it is possible to distinguish apparent (bulked and tapped), true density (crystal density) and particle density.

Bulk density of a powder is the ration of the mass of an untapped powder sample to its volume, including the contribution of the interparticulate void volume. The **tapped density** is an increased bulk density attained after mechanically tapping a graduated cylinder containing the powder sample.

Particle density includes intraparticulate pores It is possible to use gas displacement method (pycnometer density) or mercury porosimeter density (granular density) to evaluate particle density.

True density or so-called crystal density comprises exclusively the solid fraction of the material, exclusive of all voids that are not a fundamental part of the molecular packing arrangement.

For the mixtures of initial substances corresponding to the composition of the resulting set of particles (granules, micro- and nanoparticles), the true density is determined using helium pycnometer. The difference between the true density and particle density determines internal porosity of particles.

Gas (helium) pycnometry

The determination of the powder density using gas pycnometer is based on the evaluation of the volume occupied by a powder of a known mass. This volume corresponds to the volume of gas replaced by the powder. In gas pycnometric density measurements, the volume determined excludes the volume occupied by open pores; however, it includes the volume occupied by sealed pores or pores inaccessible to the gas. The density of solid is then expressed in grams per cubic centimetre (g/cm^3).

The most commonly used gas for the determination of the pycnometer density is helium due to its high ability to penetrate small open pores. The selection of gas influences the density

value as the gas penetration is dependent on the pore size as well as on the diameter of gas molecules.

In general, it can be stated that evaluation of density using gas pycnometer is a simple method possessing a lot of advantages, e.g. non-destructive test, good reproducibility and reliability.

Gas (helium) pycnometer consist of (Figure 1):

- sealed test vessel of a given volume connected by a valve to an expansion vessel of a reference volume
- equipment capable to fill the test vessel with the measuring gas until a defined pressure is reached (measured by manometer)
- connection of the system to the measuring gas source (preferably helium)

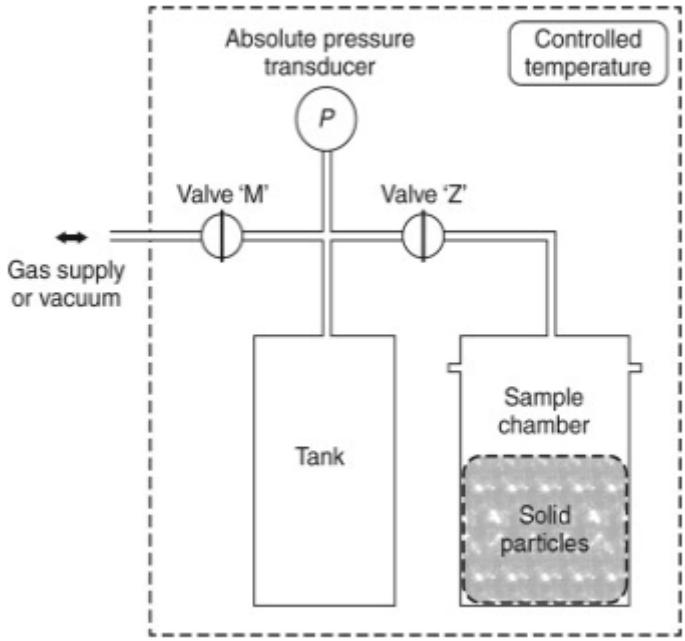

Figure 1: Schema of a gas pycnometer

Porosimetry

Porosimetry is an analytical technique used to determine material´s pore structure, in particular pore volume, pore size and pore size distribution. The term porosity refers to the total pore volume of a substance expressed in % and calculated using total volume of the substance (V_c) and its pore volume (V_p) (equation 1).

$$porosity = \frac{V_p}{V_c} \cdot 100$$

(1)

Intraparticle porosity is determined in pellets, granular powders, tablets etc. Intraparticle porosity can be calculated using the density of the whole unit and density of individual particles (components) according to the equation:

$$itraparticle\ porosity = (1 - \frac{\rho\ _{whole\ unit}}{\rho\ _{individual\ particles}}) \cdot 100$$

(2)

Interparticle porosity is defined as a ratio of the gas volume (i.e. volume of air filling the void spaces between the particles at their closest arrangement) and total volume of particles. The interparticle porosity can be determined using equation 3.

$$interparticle\ porosity = (1 - \frac{\rho_{tapped}}{\rho_{pycnometic}}) \cdot 100$$

(3)

Information about the dimensions of pores, pore types (Figure 2) and pore size distribution is possible to obtain using:

- hysteresis loops of adsorption isotherms (adsorption hysteresis)
- optical methods
- porosimetry by mercury intrusion

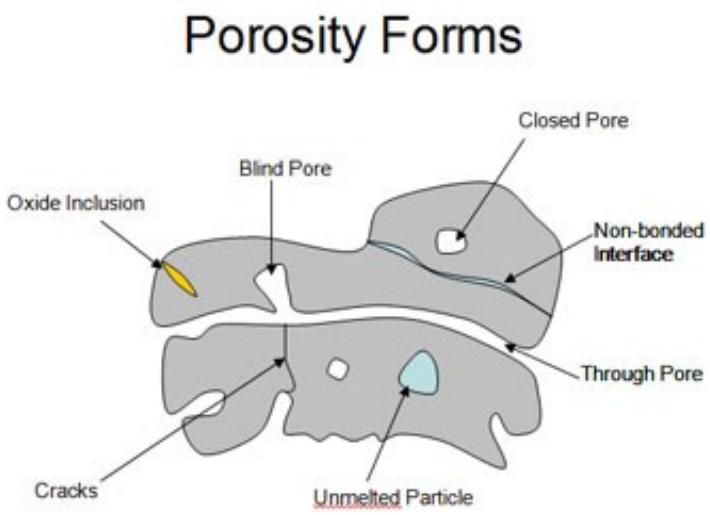

Figure 2: Pore types

Porosimetry by mercury intrusion (mercury porosimetry)

Mercury porosimetry is a popular technique which is based on the principle that the pressure required to force a nonwetting liquid such as mercury, into pores, against the resistance of liquid surface tension, is indicative for the pore size, assuming the pores are cylindrical in shape. As can be seen in Figure 4, at ambient pressure, the sample is enveloped by mercury (A). As mercury pressure increases, the large pores (1) are filled with mercury first (B). Pore sizes and pore volume distribution by pore size are calculated as the mercury pressure increases (Laplace-Young equation- the radius of the filled pore is inversely proportional to the applied pressure). At higher pressures (C), mercury intrudes into the fine pores (2) and when the pressure reaches a maximum, total open pore volume and porosity are calculated. The closed pores (3) are neglected as they are not intruded with mercury.

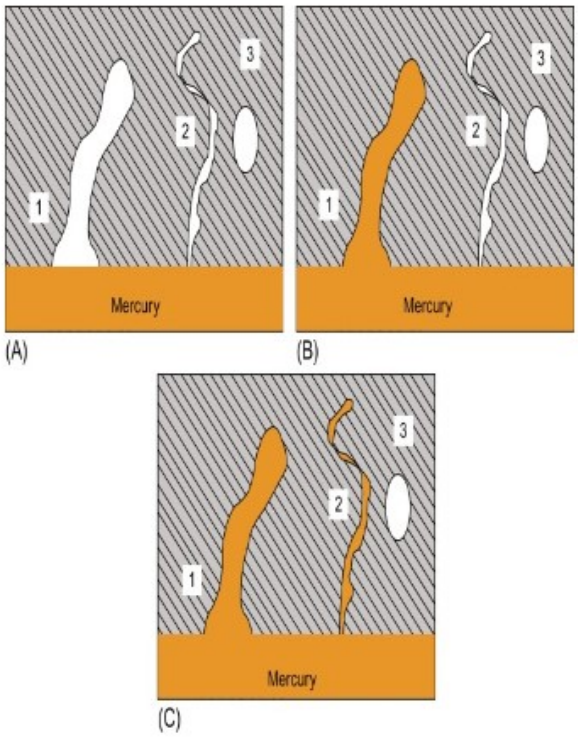

Figure 4: Mercury porosimetry technique for pore size evaluation.

Although the method is very popular, it has a number of disadvantages:

- toxicity of mercury (special storage and handling procedures)
- the sample must be inert to mercury
- contamination of the sample
- contamination of mercury

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