Application Note 20

Bulk and Skeletal Density Computations for the AutoPore

Mercury porosimetry as performed by the AutoPore is primarily intended to measure the total volume of pores within a sample between an upper and lower limit of pore sizes with a 1% accuracy level. In addition to porosity, mercury porosimetry also is often used to measure the *bulk density* and the *skeletal density*.

Relative to mercury porosimetry, bulk density is defined as the unit weight per unit volume (usually grams per cubic centimeter) of a material after the volume of the largest open pores (larger than a specific size) has been subtracted. A typical value for the largest pore included in the bulk density is 180 micrometers (μm). Skeletal density is usually computed after the volume of all pores larger than about 0.005 μm has been excluded from the volume presumed occupied by the material.

It is obvious that the mercury porosimeter does not measure density directly, but instead is primarily a volume-measuring instrument. The conversion to densities requires that the operator provide the necessary weights to complete the computation. An understanding of the bulk density and skeletal density computations will be much easier if the concept of the mercury porosimeter as a volume-measuring device is kept in mind.

Computations

A derivation of the formulas for bulk and skeletal densities begins by referring to Figure 1, a simplified sketch of a penetrometer assembly
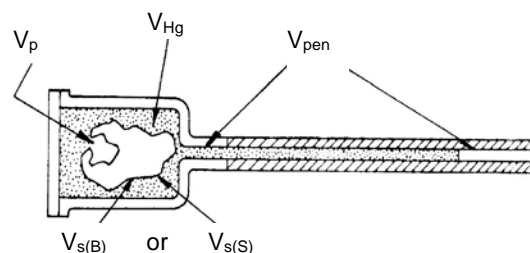

Figure 1. Penetrometer Diagram

containing a porous sample. The internal volume of the penetrometer, including both the bulb and capillary, has been previously determined by the technique of mercury filling and weighing. Assume that now the sample has been inserted and the mercury has filled all the remaining volume except that occupied by the sample and its pores of less than approximately 180 μm in opening diameter. We can now write

$$V_{s(B)} = V_{pen} - V_{Hg} \qquad (1)$$

where

$V_{s(B)}$	=	bulk volume of the sample,
V_{pen}	=	total internal volume of the penetrometer, and
V_{Hg}	=	volume of mercury occupying the remaining space.

The operating procedures for the mercury porosimeter require the weights of 1) the empty penetrometer assembly including the sealing

hardware, 2) the sealed penetrometer with only the sample inside, and 3) the sealed penetrometer with the sample inside and filled with mercury. These weights make it possible to find the volume of mercury occupying the remaining space around the sample. It is

$$V_{Hg} = \frac{W_{Hg}}{\rho_{Hg}} \quad (2)$$

where

W_{Hg} = the weight of the mercury occupying the remaining space around the sample, and

ρ_{Hg} = the density of mercury at 25 ºC (13.5335 g/cc).

The mercury weight is

$$W_{Hg} = W_{PSHg} - W_{pen} - W_s \quad (3)$$

where

W_{PSHg} = the total weight,
W_{pen} = the penetrometer and hardware weight, and
W_s = the sample weight.

W_{pen} and W_s have been provided already added together by the operator and ready to subtract from the total weight.

Substituting (3) into (2) gives

$$V_{Hg} = \frac{W_{PSHg} - W_{pen} - W_s}{\rho_{Hg}} \quad (4)$$

Also substituting (4) into (1) gives

$$V_{s(B)} = V_{pen} - \left[\frac{W_{PSHg} - W_{pen} - W_s}{\rho_{Hg}} \right] \quad (5)$$

From here it is a simple step to divide the sample weight W_s by $V_{s(B)}$ to give the bulk density $\rho_{s(B)}$.

$$\rho_{s(B)} = \frac{W_s}{V_{s(B)}} \quad (6)$$

The skeletal volume $V_{s(S)}$ is found by subtracting the total volume of pores filled by mercury V_p from the bulk volume.

$$V_{s(S)} = V_{s(B)} - V_p \quad (7)$$

Specific pore volume, P_s, the pore volume per gram of material is most commonly reported. It is then necessary to multiply the specific pore volume by the total weight of the sample to obtain the total pore volume.

$$V_{s(S)} = V_{s(B)} - W_s P_s \quad (8)$$

Again, it is only necessary to divide the sample weight by $V_{s(S)}$ to obtain the skeletal density.

$$\rho_{s(S)} = \frac{W_s}{V_{s(S)}} \quad (9)$$

Troubleshooting

Errors and poor results sometimes occur in density determinations by mercury porosimetry. The most likely reason for poor results is apparent in Equation (5). Notice that $V_{s(B)}$ is most commonly a small number derived by subtracting two larger numbers which are nearly equal. It is not uncommon for these numbers to be 10 times greater than $V_{s(B)}$. One percent errors in the numbers become ten percent errors in $V_{s(B)}$. All the numbers for computing $V_{s(B)}$ are supplied by the operator and are derived primarily from weighing procedures. (V_{pen} is usually obtained by weighing the penetrometer after filling it with mercury, and dividing the weight by the density of mercury at ambient temperature.)

The major opportunity for instrument error to affect $V_{s(B)}$ is in the filling process. Should the penetrometer not be completely filled, the excess volume is assigned to the sample. Some slight error could also occur due to temperature differences as the density of mercury is assumed by some instruments to be constant at 13.5335, the 25 °C value. The exact pressure applied to the mercury at the starting point for the pore volume measurement also affects the bulk volume as higher pressures fill progressively smaller pores. If the material has a significant pore volume distribution in the 100-µm range, it will be difficult to obtain reproducible bulk volume measurements due to the requirement for a highly precise and reproducible starting pressure.

Accurate skeletal volume $V_{s(S)}$ measurement is dependent upon, first, the accuracy of $V_{s(B)}$ and then upon the accuracy of the pore volume measurement. It is not, however, as dependent upon the starting pressure since any pore volume not intruded at the low filling pressure (and thereby increasing $V_{s(B)}$)will be intruded by mercury, measured, and subtracted as the pressure increases. The error thereby is self-cancelling.

Mismatches of measured skeletal densities to handbook values for the material may also be due to closed pores to which mercury has no access, pores that are too small to be intruded by mercury at the highest pressure used, and compression of the sample. Compression can be particularly significant in the case of organic materials. Up to 10% volume reduction can occur in plastic materials at 60,000 psia. An accompanying change of density occurs and is reported by the instrument.

Recommendations

Listed below are some recommendations to help minimize errors:

- Ensure accurate weighing to at least 5 significant digits when possible.

- Accurately determine the internal volume (bulb and capillary) of the penetrometers to five significant digits if possible. Be sure to use the same sealing cap with the penetrometer at all times since slight irregularities from cap to cap can cause measurable errors in the internal volume.

- Occasionally inspect penetrometers to make sure they are properly filling.

- Avoid precise density measurements when the temperature of the penetrometer will vary significantly.

- Use the maximum practical sample volume in the penetrometer bulb consistent with capillary capacity. This will improve the mathematical "leverage."

- Carefully review weight information prior to each analysis to help prevent errors.

- Examine the pore volume distribution curve for high slope at the beginning and end. Reproducible results will be more difficult to obtain in such cases. Slope at the high-pressure end may also be due to crushing of closed pores or compression of the material.