Density and porosity

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Density and porosity

Density: terms
• Bulk density
• True density
• Theoretical density
• Apparent density

Porosity: terms
• Total porosity
• Open porosity
• Close porosity
Bulk density

- Bulk density = อัตราส่วนมวลรวมต่อปริมาตรทั้งรวมรูพรุนด้วย หรือ ปริมาตรจ้าเฉพาะ
- Bulk density ของชิ้น Ceramic มักเป็นปริมาตรที่มีรูพรุนด้วย ซึ่งรวมรูพรุนแบบเปิด และแบบปิด (bulk volume/external volume)
- Bulk density ≠ True density

$\text{Bulk density} = \frac{\text{Mass}}{\text{Total volume (A + B + C)}}$

$\text{Bulk volume} = A + B + C$

$A = \text{solid volume or True volume} \sim \text{Theoretical density}$

$B = \text{Open pore volume}$

$C = \text{Closed pore volume}$

Bulk volume $\rightarrow$ วัสดุเม็ด ที่บรรจุไปแต่ละเม็ดในกระท่อม
Apparent density ความหนาแน่นปรากฏ

\[
\text{Apparent density} = \frac{\text{Mass}}{\text{Apparent volume} (A + C)}
\]
Density

True density = \frac{mass}{true \ volume}

Apparent density = \frac{mass}{apparent \ volume \ (A + C)}

Bulk density = \frac{mass}{bulk \ volume \ (A + B + C)}

Theoretical density = \frac{mass \ of \ a \ unit \ cell}{volume \ of \ a \ unit \ cell}
Theoretical density

- Theoretical density (TD) is the mass of a substance divided by its volume. It is an inherent property of the substance and is independent of the state or physical conditions under which it is measured.

- X-ray density is the mass of a substance divided by its volume, calculated from X-ray measurements.

- X-ray density is used to calculate the unit cell volume and is calculated by dividing the number of atoms in the unit cell by the unit cell volume.

Example: Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ is Fluorite structure: 4 cation sites, 8 anion sites (4(ZrO$_2$)/unit cell), unit cell parameter = 5.131 Å

\[
TD = \frac{4(0.85 \text{ Zr}) + 4(0.15 \text{ Ca}) + 4(1.85 \text{ O})}{6.03 \times 10^{23} (5.131 \text{ Å})^3 (10^{-24})} = 5.480 \text{ g/cm}^3
\]

\[
\% \text{ theoretical density} = \frac{\text{bulk density}}{\text{true density}} \times 100
\]

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Liquid pycnometer techniques: true density

\[ \rho = \frac{W_2 - W_1}{(W_4 - W_1) - (W_3 - W_2)} \]
Archimedes method

- Bulk volume
- Bulk density
- Apparent volume
- Apparent density
Density ต่างๆ

**Apparent solid Volume** = the difference between dry weight (D) and the immersed weight (I) of piece.

- S – I = volume of open pores + sealed pores + solid
- S – D = Vol. open pores
- D – I = Vol. of sealed pore + solid

**Bulk density**

\[
\text{Weight} = \frac{D}{\text{App. Vol.}} = \frac{D}{S - I}
\]

**True density** = \[
\frac{\text{Weight}}{\text{True Vol.}}
\]

**Apparent solid density** = \[
\frac{\text{Weight}}{\text{App. – solid Vol}} = \frac{D}{D - I}
\]

Where
- D = wt. Of dry piece (g)
- S = wt. Of soaked piece (g)
- I = wt. Of soaked immersed piece (g)
Porosity

- Open pores
- Close pores
- Techniques:
  - Archimedes
  - Instrument
Porosity

Apparent Porosity = Ratio of open pore volume to total volume
% App. Porosity = \( \frac{\text{open pore vol.}}{\text{Total vol.}} \times 100 \)
= \( \frac{S - D}{S - I} \times 100 \)

Water absorption = Ratio of open pore vol. to weight of the test piece
% Water absorption = \( \frac{\text{open pore vol.}}{\text{wt.}} \times 100 \)
= \( \frac{S - D}{D} \times 100 \)
True porosity

% True Porosity = Volume of all pores \times 100
Total vol. of the test piece = App. Vol – True vol \times 100

% True Porosity = \left(1 - \frac{\text{True Vol.}}{\text{App. Vol.}}\right) \times 100

True Vol./App. Vol. = \frac{\text{weight}}{D_t} \div \frac{\text{weight}}{D_a} = (1 - \frac{D_a}{D_t}) \times 100

where

\( D_a \) = Apparent density = \frac{\text{weight}}{\text{App. Vol.}}

\( D_t \) = True density = \frac{\text{weight}}{\text{True. Vol.}}

% True porosity = 1 - \frac{S_a}{S_t} \times 100

\( S_a \) = Apparent specific gravity
\( S_t \) = True specific gravity
Pore volume measurement

- Gas absorption เมื่อ pore น้อยขนาด < 800Å
- Mercury penetration (Porosimeter techniques) เมื่อ ขนาด pore > 800 Å

Pore size limits of gas adsorption (BET) and mercury intrusion porosimetry

John I. D’Souzae
Gas adsorption → BET

- ถ้า monolayer adsorption ใช้ low $P/P_0$ ratio
- ถ้า multilayer adsorption ใช้ $P/P_0$ 0.05-0.3
- ถ้า higher pressure gas จะเกิดการ condense กลายเป็น ของเหลว $P/P_0$ 0.6-0.99
BET equation

Support that gas condense in cylindrical capillaries with radius \((r)\) and pressure in capillaries \((P)\).

Kelvin equation

\[
\ln \frac{P}{P_0} = \frac{2\gamma_{LV} V_L \cos \theta}{RTr}
\]

\(P_0\) = saturated gas pressure of liq. on plane surface

\(\gamma_{LV}\) = surface tension liq.- vapor interface

\(V_L\) = molar volume of liquid

\(\theta\) = contact angle between liq. and pore wall

\(R\) = gas constant \((8.31\text{ kJ}/\text{K.mol})\)

\(T\) = adsorption temperature
BET equation

\[ N_2 \text{ gas, at boil point (77 K)} \]

\[ \gamma_{LV} = 8.72 \times 10^{-3} \frac{N}{m^2} \]

\[ V_L = 34.68 \times 10^{-6} \frac{m^3}{mol} \]

\[ \theta = 0 \]

\[ r = \frac{2 \gamma_{LV} V_L \cos \theta}{RT \ln \frac{P}{P_0}} = \frac{4.05 \times 10^{-4}}{\log \frac{P}{P_0}} \mu m \]

ถ้าทราบค่า \( P/P_0 \) สามารถหาค่า \( r \) ได้ ค่า \( P/P_0 \) ที่เหมาะสมคือ 0.6-0.99 จะได้ค่า \( r \) 2-100 nm
Mercury porosimeter

- % porosity,
- pore volume distribution,
- pore size distribution,
- surface area distribution,
- particle size distribution,
- bulk and apparent density.
Phenomenon of capillary rise

\[ \theta = \text{contact angle} \]

- Water wet the well
  - \( \theta < 90^\circ \) (wetting liq.)

- Hg wet the well
  - \( \theta > 90^\circ \) (non-wetting liq.) \rightarrow depressed
Mercury porosimeter

- placing a sample into a container,
- evacuating the container to remove contaminant gases and vapors (usually water) and, while still evacuated, allowing mercury to fill the container. (a solid, a non-wetting liquid (mercury), and mercury vapor)
- Next, pressure is increased toward ambient while the volume of mercury entering larger openings in the sample bulk is monitored.
- When pressure has returned to ambient, pores of diameters down to about 12 mm have been filled.
- The sample container is then placed in a pressure vessel for the remainder of the test. A maximum pressure of about 60,000 psia (414 MPa) is typical for commercial instruments and this pressure will force mercury into pores down to about 0.003 mm in diameter.
- The volume of mercury that intrudes into the sample due to an increase in pressure from $P_i$ to $P_{i+1}$ is equal to the volume of the pores in the associated size range $r_i$ to $r_{i+1}$, sizes being determined by substituting pressure values into Washburn’s equation.
Mercury porosimeter

- **pore diameter**, total **pore volume**, **surface area**, and bulk and absolute **densities**.

- The technique involves the intrusion of a **non-wetting** liquid (often **mercury**) at high **pressure** into a material through the use of a **porosimeter**.

- The pore size can be determined based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid’s surface tension.

- A known as **(Washburn’s equation)** for the above material having **cylindrical** pores is given as:
  
  \[ P_L - P_G = \frac{4\rho \cos \theta}{D_p} \]

  - \( P_L \) = pressure of liquid
  - \( P_G \) = pressure of gas
  - \( \sigma \) = surface tension of liquid
  - \( \theta \) = contact angle of intrusion liquid
  - \( D_p \) = pore diameter
Mercury porosimeter

Since the technique is usually done under vacuum, the gas pressure begins at zero. The contact angle of mercury with most solids is between 135° and 142°, so an average of 140° can be taken without much error. The surface tension of mercury at 20 °C under vacuum is 480 mN/m. With the various substitutions, the equation becomes:

\[ D_P = \frac{213}{P_L} \]

As pressure increases, so does the cumulative pore volume. From the cumulative pore volume, one can find the pressure and pore diameter where 50% of the total volume has been added to give you the median pore diameter.
Nitrogen gas adsorption
Mercury Porosimeter

Log Differential Intrusion vs Pore size

- Log Differential Intrusion
- Cumulative Intrusion

Pore size Diameter (nm)

Log Differential Intrusion (mL/g)

Cumulative Intrusion (mL)

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