Journal of the European Ceramic Society 17 (1997) 753–757

PII: S0955-2219(96)00181-1
0955-2219/97/$17.00

Reliability and Reproducibility of Mercury Intrusion Porosimetry

G. de With & H. J. Glass

Eindhoven University of Technology, CTK, 5600 MB, Eindhoven, The Netherlands

(Received 2 February 1995; revised version received 21 August 1996; accepted 29 August 1996)

Abstract

Precise interpretation of mercury intrusion data is only possible for cylindrical pores. Nevertheless reproducible data can be obtained which compare well with results on cylindrical pores from independent image analysis experiments. The effect of the compressibility correction is shown to be small. © *1997 Elsevier Science Limited. All rights reserved.*

1 Physical Homogeneity

In view of the influence of physical homogeneity on the properties of ceramic products, it is necessary to characterize the microscopic physical homogeneity experimentally. Measuring pore size distributions during processing provides insight into the evolution of the physical homogeneity. The pore size distribution is conveniently measured with mercury intrusion porosimetry (MIP). MIP uses the non-wetting property and high surface tension of liquid mercury: mercury will not flow into (small) cavities, pores or cracks spontaneously unless pressure is applied. Therefore the volume of intruded mercury at one pressure is a result of penetration into all pores larger than a particular size. The cumulative pore volume measured in this way as a function of pressure constitutes the raw data. This intruded volume of mercury has to be interpreted in terms of pore size and shape. The objective of this note is to analyze the reliability and reproducibility of the pore size measure as obtained from the raw data determined with this technique. A detailed list of applications of porosimetry is provided by Whittemore,[1] while van Brakel *et al.*[2] present a list of limitations and capabilities.

2 Thermodynamic Derivation of the Intrusion Equation

Pores are modelled as simple non-connected channels which are penetrated by mercury. A three-phase system solid(s)/vapour(v)/liquid(l) thus exists. The condition of equilibrium states that the mechanical work dW should balance the change in surface energy dG:

$$dW = PdV = dG = \gamma_{sl}dA_{sl} - \gamma_{sv}dA_{sv} + \gamma_{lv}dA_{lv} \quad (1)$$

where P is the pressure difference, dV the volume change, γ is the surface energy at the various interfaces and dA the change in interfacial area. In the following, the surface energy is assumed to be equal to the surface tension. During intrusion, the area of the solid covered with mercury is equal to the area originally covered with gas so that $A_{sl}=A_{sv}\equiv A$. This simplifies dG to:

$$dG = (\gamma_{sl} - \gamma_{sv})dA + \gamma_{lv}dA_{lv} \quad (2)$$

while the three surface tensions are related by the Young–Dupré equation:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos(\theta) \quad (3)$$

This yields:

$$PdV = \gamma_{lv}(-\cos(\theta)dA + dA_{lv}) \quad (4)$$

The quantity dA_{lv} is usually assumed to be zero, i.e. the area and shape of the cross-section is constant, since inadequate information on the change of cross-sectional area is available. Accordingly, with $\gamma'\equiv\gamma_{lv}\cos(\theta)$:

$$P = -\gamma' dA/dV \quad (5)$$

Therefore for pores with a cross-section of constant shape (and neglecting the contribution of transitions between sizes), a general expression for the change in area dA and in volume dV is given by:

$$dA = \alpha_A r l(r)\,dr \text{ and } dV = \alpha_v r^2 l(r)\,dr \quad \text{or } dA/dV = \alpha_A/(\alpha_v r) \quad (6)$$

where α_A and α_v are shape-dependent constants and $l(r)$ the length of pores with size r. The ratio

α_A/α_v effectively represents a shape factor characterizing the geometry of the pore. In general, the pores are assumed to be cylindrical. If we associate r with the radius, the shape factor α_A/α_v equals 2. Consequently, the pressure P becomes:

$$P = -2\gamma'/r = -2\gamma \cos(\theta)/r \quad (7)$$

where from now on we omit the subscript lv for γ. This equation corresponds to the equation originally proposed by Washburn,[3] which is the most widely applied intrusion equation.

3 Geometric Derivation of the Intrusion Equation

The application of MIP is extended if it is possible to derive an indication of the shape of the pores or if a shape other than the cylindrical shape can be used for the interpretation. In order to assess the importance of the shape factor α_A/α_v, an alternative derivation is considered. Applying the Young–Laplace equation for pressure differences P over any curved surface S with r_1' and r_2' the principal radii of curvature of the interface between mercury and vapour, leads to:

$$P = \gamma \int (1/r_1' + 1/r_2')dS / \int dS = \gamma (1/r_1' + 1/r_2') \quad (8)$$

where the last equation follows from the mechanical equilibrium condition. Solution of eqn (8) requires information on the shape of the boundary of the (pore) cross-section. In the case of a circular cross-section, the principal radii are given by:

$$r_1' = r_2' = r/\cos(\theta) \quad (9)$$

where r denotes the principal radius of curvature of the pore. Substituting r_1' and r_2' in eqn (13) with eqn (14) and recognizing that r is a constant, yields:

$$P = -2\gamma \cos(\theta)/r \quad (10)$$

The derivation shows that, for pore shapes other than the cylinder, a spatial description of the mercury meniscus is required in order to solve eqn (8).

If we assume that the cross-sections of the pores are regular polygons and that mercury penetrates a pore up to the inscribed circle with radius r, Table 1 shows that $dA/dV = 2/r$ always holds. Only at a pressure larger than given by eqn 10, the area between the inscribed circle and the true shape will be filled. This effect shows as the apparent presence of smaller pores. This smearing effect (and the neglect of dA_{lv}) does not warrant a more sophisticated interpretation of the pore size than the inscribed radius.

4 Experimental

All measurements were performed with the Micromeritics 9310 PoreSizer. The resolution of the AD convertor was such that the smallest measuring interval is about 0·15% of the total measuring range of 200 MPa. This restricts the number of data points to 670, which is one of the limiting factors in the accuracy of the experimental PSD.

The pore size distribution (PSD) is defined as the differential volume of pores V as a function of the pressure P:

$$\text{PSD} = dV/dP \quad (11)$$

Recognizing that $P = -2\gamma \cos(\theta)/r$ results in:

$$\text{PSD} = (r^2/2\gamma \cos(\theta))\, dV/dr \quad (12)$$

Note that physical significance of the dimension of the PSD, [m^5/N], is unit volume per unit pressure.

The surface tension γ and contact angle θ vary according to the chemical nature of the sample and its structure. Though no consensus exists in the literature, $\gamma = 48{\cdot}5\ 10^{-2}$ N/m and $\theta = 130°$ are generally adopted. The use of these values yields good correspondence when comparing the average pore size determined with MIP and SEM.[2,4,5]

5 Accuracy and Reproducibility of MIP

A limiting factor in the accuracy of the PSD is the expansion of the glass burette and compression of the mercury and the sample. By measuring the intrusion without a sample, the net effect of the glass expansion and mercury compression is found as a function of pressure. Sample compression is only measurable if the sample is non-porous.

The effect of compressibility can be corrected by calculating the coefficients of compressibility. Throughout the pressure range of interest (1–2000 bar),

Table 1. Shape factors for pores with a regular polygon cross-section

Cross-section		*Pore*	
Boundary	$B = 2nr \tan(\pi/2)$	Area	$A = Bl$, $dA = 2nr \tan(\pi/2)\, dl$
Area	$O = nr^2 \tan(\pi/2)$	Volume	$V = Ol$, $dV = nr^2 \tan(\pi/2)\, dl$

Pore modelled as a n-sided polygon with inscribed radius r and length l.

the isothermal compressibility coefficient β can be assumed to vary linearly[6] with the pressure P:

$$\beta = -1/V(dV/dP)_T = \beta_0 + \beta_1 P \quad (13)$$

Integration with respect to pressure and expansion of $\ln(V/V_0)$ in a Taylor series up to second order yields:

$$\Delta V = (\beta_0 P + \beta_1 P^2/2)V_0 \quad (14)$$

where $\Delta V=(V-V_0)/V_0$. The volume change due to compressibility is due to both mercury and glass:

$$\Delta V(\text{overall}) = \Delta V(\text{mercury}) - \Delta V(\text{glass}) \quad (15)$$

The individual contributions are represented by eqn (14), so that eqn (15) contains four parameters. However, the coefficients for mercury were taken from literature[7] and kept constant:

$$\beta_0(\text{mercury}) = (4{\cdot}02 \pm 0{\cdot}02)10^{-11}\ \text{Pa}^{-1}$$
$$\beta_1(\text{mercury}) = (1{\cdot}3 \pm 0{\cdot}2)10^{-20}\ \text{Pa}^{-2}$$

The volume of mercury intruded in the burette as a result of compression was fitted to eqn (15) using the least-squares criterion. The following compressibility coefficients β for the glass of the burette were determined:

$$\beta_0(\text{glass}) = (2{\cdot}85 \pm 0{\cdot}11)10^{-11}\ \text{Pa}^{-1}$$
$$\beta_1(\text{glass}) = (0{\cdot}0 \pm 0{\cdot}6)10^{-20}\ \text{Pa}^{-2}$$

The validity of this approach can be verified by determining the compressibility of the glass with the pulse-echo technique. For this purpose, a planoparallel sample from burette glass was prepared and the longitudinal wave velocity v_l and transverse wave velocity v_s were measured at 10 and 5 MHz respectively yielding v_l = 5·542 km/s and v_s = 3·466 km/s. The loss tangent was found to be smaller than 0·15, so no correction for damping is required. The compressibility β was calculated from these values (density of the glass 2·22 g/cm^3) using the conventional formula for isotropic materials. The resulting value for β_0, 3·09 10^{-11} Pa^{-1}, compares favourably with the value determined from MIP and gives confidence in the analysis.

The compressibility β of non-porous solids may be determined by extending eqn (15) to:

$$\Delta V = \Delta V(\text{Hg}) - \Delta V(\text{glass}) + \Delta V(\text{sample}) \quad (16)$$

When the βs of glass and mercury are known, the remaining volume change can be attributed to compression of the sample. The compressibility of the sample is also characterized with β_0 and β_1. Using two fully dense synthetic materials, polyethylene (PE) and rubber, the accuracy of this technique is investigated. The following coefficients have been determined with MIP:

$$\beta_0(\text{PE}) = (4{\cdot}43 \pm 0{\cdot}32)\ 10^{-10}\ \text{Pa}^{-1}$$
$$\beta_1(\text{PE}) = (-1{\cdot}5 \pm 0{\cdot}1)\ 10^{-18}\ \text{Pa}^{-2}$$
$$\beta_0(\text{Rubber}) = (2{\cdot}06 \pm 0{\cdot}26)10^{-8}\ \text{Pa}^{-1}$$
$$\beta_1(\text{Rubber}) = (-4{\cdot}5 \pm 0{\cdot}7)\ 10^{-17}\ \text{Pa}^{-2}$$

Comparison with literature values shows good correspondence considering the large range of chemical compositions of PE and rubber.[6,7]

$$\beta_0(\text{PE}) = 3{\cdot}2 \times 10^{-10}\ \text{Pa}^{-1}$$
$$\beta_1(\text{PE}) = -2{\cdot}5 \times 10^{-18}\ \text{Pa}^{-2}$$
$$\beta_0(\text{Rubber}) = 2{\cdot}0 \times 10^{-8}\ \text{Pa}^{-1}$$
$$\beta_1(\text{Rubber}) = -5{\cdot}0 \times 10^{-17}\ \text{Pa}^{-2}$$

After correcting for the compressibility of mercury and glass, the accuracy of MIP was further analysed using a filter membrane (ANOTEC Separations). SEM photos taken perpendicular to the surface indicate that these membranes have a regular pore structure with a narrow pore size distribution. The median pore size of three types of membranes was determined with MIP and image analysis of SEM photos. With the latter, the pore size was determined by averaging the size of 100 randomly intersected pores, corrected to diameters. The results are given in Table 2 and show that the differences between the direct (image analysis) and indirect determination (MIP) of the mean pore size are about 1–2%. Therefore, the MIP technique gives an accurate impression of the pore size (distribution). Furthermore, the limited influence of the compressibility correction is clearly demonstrated.

The reproducibility of MIP for real compacts was determined by measuring the pore size distribution of a series of nine (Mn,Zn)–ferrite compacts with identical densities (Table 3). The density ρ of the compact can be found from mass m and sample volume V or from the theoretical

Table 2. Determination of accuracy of MIP

*Specified size** (μm)	*Measured pore size MIP, corrected* (μm)	*Image analysis* (μm)	Δ (%)	*MIP, uncorrected* (μm)
0·02	0·0738	0·0743	0·7	0·0730
0·1	0·1020	0·1032	1·2	0·1015
0·2	0·1139	0·1160	1·8	0·1137

*Specified size deviated considerably from image analysis size for 0.02 μm.

Table 3. Reproducibility of compaction and MIP

	Mean	*Standard deviation*	*Variation (%)*
Pore size	0·1282 μm	0·0030 μm	2·3
Density	2·649 g/cm^3	0·038 g/cm^3	1·4

Acrylic binder, compact diameter 14·1 mm, height 2·0 mm, compaction pressure 125 MPa.

density ρ_{th} combined with the total sample and pore volume:

$$\rho = m/V \text{ or } \rho = \rho_{th}\,(V-V_p)/V \qquad (17)$$

where V_p is the total pore volume of the sample. Comparison of the densities indicates whether all pores are intruded during a MIP measurement. Table 3 shows that the reproducibility of average pore diameter as determined by MIP measurements is about 2%. This reproducibility percentage is comparable to that reported by Moscou and Lub.[8] Moreover, there is good agreement (~1–2%) between the density as determined by porosimetry and from mass and volume.

6 Discussion

Several aspects have to be considered if one discusses porosimetry. The most important ones are addressed below.

6.1 Interpretation of size

The present analysis shows that accuracy in porosimetry can be reached if (nearly) cylindrical pores are present, as confirmed by image analysis. The results are in line with other work. Cebeci,[9] for example, showed that conical pores result in larger diameters while spherical pores yield larger or smaller pore diameters, depending on the entrance size. Moreover, Lapidus *et al.*[10] explicitly showed that the pore entrance distribution is actually measured in porosimetry.

6.2 Lost porosity

If all pores are measured, the porosity as determined by porosimetry should agree with independent measurements, e.g. from dimensions, weight and density. This appeared to be true for the ceramic compacts used here for the reproducibility experiments. In other types of materials, however, a significant percentage of 'lost' pores can be observed. Alford *et al.*[11] reported 30–50% not intruded pores in hardened cement pastes. This porosity consisted typically of spherical large macropores larger than 15 μm. In ceramic compacts these pores should be rather scarcely present. The origin of lost porosity can be found in inaccessibility (closed pores) and/or sizes out of the measuring range. The lower limit is given by the maximum applied pressure (typically 200 MPa resulting in ~4 nm), while the upper limit is given by the minimum applied pressure (either 1 bar (atmospheric) resulting in ~15 μm or vacuum resulting in ~1 mm).

6.3 Data and damage

The proper values for γ and θ to be used have been extensively discussed.[4–6] The values adopted here are frequently used. In view of the good agreement between the image analysis and porosimetry data of the present experiments at least the value of the product $\gamma \cos(\theta)$ seems to be correct. In some cases damage introduced in the specimens by the porosimetry itself has influenced the pore size distribution. Since in this case only open porosity is present, the damage introduced is considered negligible.

6.4 Hysteresis

The measurement of extrusion curves show that hysteresis occurs but also that the reproducibility of hysteresis is poor. This has been attributed to a few larger pores dominating extrusion,[12] in which case the use of extrusion data can be seriously doubted, or to contact angle hysteresis for more homogeneous compacts.[13]

7 Final Remarks

Summarising, we conclude that, although the precise interpretation of the MIP data for non-cylindrical pores is difficult, the method yields reproducible results, which correspond well with results on cylindrical pores obtained from independent image analysis experiments. The analysis given indicates that for an accurate MIP measurement the pores should have a constant size and shape. The effect of the compressibility correction is shown to be small.

References

1. Whittemore, O. J., Mercury porosimetry of ceramics. *Powder Techn.*, **29** (1981) 167–172.
2. van Brakel, J., Modry, S. & Svata, M., Mercury porosimetry: State of the art. *Powder Techn.*, **29** (1981) 1–12.
3. Washburn, E., Note on a method of determining the distribution of pore sizes in a porous material. *Proc. Nat. Acad. Sci. USA* **7** (1921) 115–116.
4. Liabastre, A. & Orr, C., An evaluation of pore structure by mercury penetration. *J. Coll. Interf. Sci.*, **64** (1978) 1–18.

5. Kloubek, J., Hysteresis in porosimetry. *Powder Techn.*, **29** (1981) 63–73.
6. Huisman, H., Rasenberg, C. & van Winsum, J., An improved mercury porosimetry apparatus: Some magnetic tape applications. *Powder Techn.*, **36** (1983) 203–213.
7. *Handbook of Chemistry and Physics*, 55th edn, ed. R. Weast. CRC Press, Boca Raton, FL.
8. Moscou, L. & Lub, S., Practical use of mercury porosimetry in the study of porous solids. *Powder Techn.*, **29** (1981) 45–52.
9. Cebeci, O. Z., The intrusion of conical and spherical pores in mercury intrusion porosimetry. *J. Coll. Interf. Sci.*, **78** (1980) 383–388.
10. Lapidus, G. R., Lane, A. M., Ng, K. M. & Conner. W. C., Interpretation of mercury porosimetry data using a pore-throat network model. *Chem. Eng. Commun.*, **38** (1985) 33–56.
11. Alford, N. McN. & Rahman, A. A., An assessment of porosity and pore sizes in hardened cement pastes. *J. Mater. Sci.*, **16** (1981) 3105–3114.
12. Ciftcioglu, M., Smith, D. & Ross, S., Mercury porosimetry of ordered sphere compacts: Investigation of intrusion and extrusion pore size distributions. *Powder Techn.*, **55** (1988) 193–205.
13. Lowell, S. & Shields, J. E., Theory of mercury intrusion hysteresis. *Powder Techn.*, **38** (1984) 121–124.