A Novel Mercury Free Technique for Determination of Pore Volume, Pore Size and Liquid Permeability

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Abstract

A novel mercury free technology for measurement of liquid permeability and through pore volume, size and distribution is discussed and results obtained using commercial components have been analyzed. Mercury intrusion porosimetry, which is normally used for such measurement is shown to be inappropriate, although interesting information on pore structure may be obtained by combining measurements made by techniques.

Introduction

Sintered powdered components and powdered beds find wide applications, in which pore volume, pore size and pore distribution of through pores in these materials and liquid flow rates through these products determine the performance and efficiency of the process. Pore size and distribution determine the barrier characteristics, pore volume determine the holding capacity and liquid flow rate determines the rate of the process. For some applications, surface area of through pores is also important for controlling reaction rates. Mercury intrusion porosimetry is often used to measure pore volume and size of all pores in a porous product. However, this technique cannot measure liquid flow rate, cannot measure pore volume and size of just the through pores, and cannot avoid use of toxic materials like mercury, which causes health hazards and environmental pollution. The novel technique, liquid extrusion porosimetry does not use any toxic material to measure liquid flow rate, through pore volume and through pore size. This technique can also measure through pore surface area. Liquid extrusion porosimetry has been described. Results obtained using this technique have been discussed and compared with those obtained using mercury intrusion porosimetry.

Liquid Extrusion Porosimetry

Principle

A liquid, whose surface free energy with a material is lower than the surface free energy of air with that material is known as a wetting liquid. A wetting liquid is allowed to spontaneously fill the pores of the selected sample. The sample is placed on a membrane and loaded in the sample chamber. The membrane is such that its largest pore is smaller than the smallest pore of interest in the sample and the wetting liquid that spontaneously fills the pores of the sample also spontaneously fill the pores of the membrane. The pressure of air over the sample is slowly increased so as to displace the liquid from pores.

The pressure required to displace the liquid from a pore is found by equating the work done by the gas to the increase in surface energy [1].

$$p = 4 \gamma \cos \theta / D \tag{1}$$

where p is the pressure difference across the pore, γ is the surface tension of the wetting liquid, θ is the contact angle of the liquid with the sample and D is the pore diameter. For low surface tension wetting liquids the contact angle is taken as zero [2]. Equation 1 shows that liquid will be pushed out of the largest pore of the sample at the lowest pressure and with increasing pressure smaller pores of the sample will be emptied at higher pressures. Because the largest pore in the membrane is smaller than the smallest pore of interest in the sample, the gas pressures required to empty the pores of the sample can not remove liquid from the pores of the membrane and permit gas to pass through the membrane. However, all the liquid pushed out of the pores of the sample by the gas will pass through the membrane, while its pores remain filled with the liquid.

The sketch in Figure 1A illustrates the principle. The pressure of the gas and the amount of liquid flowing out of the membrane are accurately measured. The pressure gives pore diameter and the volume of displaced liquid gives pore volume.

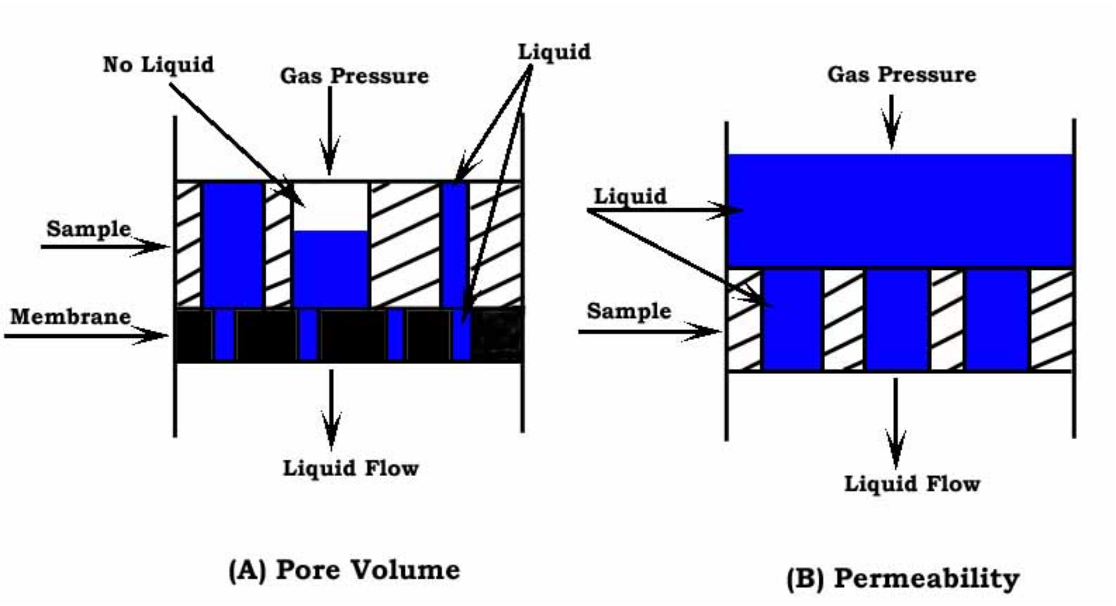

Figure 1. Sketch illustrating the principle of liquid extrusion porosimetry.

For measurement of liquid permeability, the membrane is removed and pressure on excess liquid maintained on the sample is increased (Figure 1B). The pressure and the rate of increase of the volume of the displaced liquid are measured.

Instrument

The liquid extrusion porosimeter based on the above principle was designed and built using the state-of-the-art technology. The instrument used in this study is shown in Figure 2. The fully automated instrument yielded accurate and reproducible data. Windows based test execution, data acquisition, data storage and data reduction, made the operation very simple.

Figure.2: The Liquid Extrusion Porosimeter

Mercury Intrusion Porosimetry

In this technique, the non-wetting liquid, mercury is forced into pores of the sample. The pressure needed to intrude mercury in to a pore is given by:

$$p = - 4 \gamma \cos \theta / D \qquad (2)$$

where p is pressure on mercury, γ is surface tension of mercury, θ is contact angle of mercury with the sample and D is pore diameter. The pressure on mercury and the decrease in volume of mercury due to intrusion are measured. These data are used to compute pore size, pore volume and pore volume distribution. However, the pressure required for this technique is much higher than the pressure required for liquid extrusion porosimetry, because surface tension and contact angles of mercury are very large. The PMI mercury intrusion porosimeter was used in this investigation.

Results and Discussion

Liquid Extrusion Porosimetry

A sintered ceramic powder component was investigated. Water was used as the wetting liquid. The surface tension of water was 72kJ/m^2.

Through pore diameter and volume: The pore diameters were calculated from measured differential pressure and the cumulative pore volume was calculated from the measured volume of liquid displaced from the pores. The cumulative volume of through pores (pores that permit flow) is shown as a function of pore diameter in Figure 3. This figure also gives the pressure required to displace liquid from pores of the sample. The total pore volume of through pores was 2.834cm^3/g.

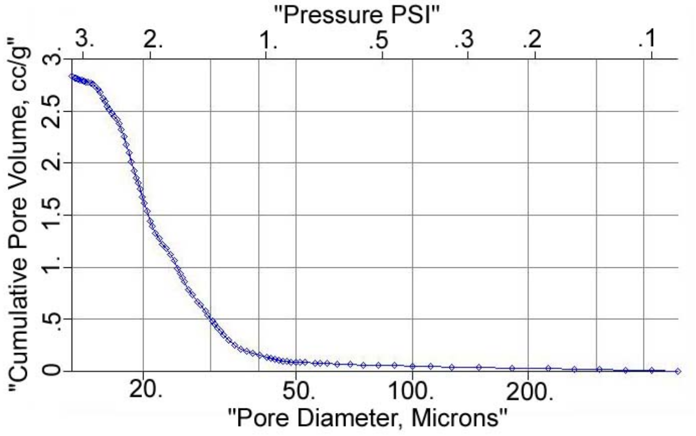

Figure 3. Cumulative pore volume measured as a function of pore diameter in liquid extrusion porosimeter.

Through pore volume distribution: The pore volume distribution function, f, is defined as:

$$f = - (dV / d \log D) \qquad (3)$$

where V is the cumulative pore volume. The distribution function is presented in Figure 4. It follows from Equation 3 that the area under the curve in a pore size range gives the volume of through pores in that range. The median pore diameter based on volume is 21.00µm.

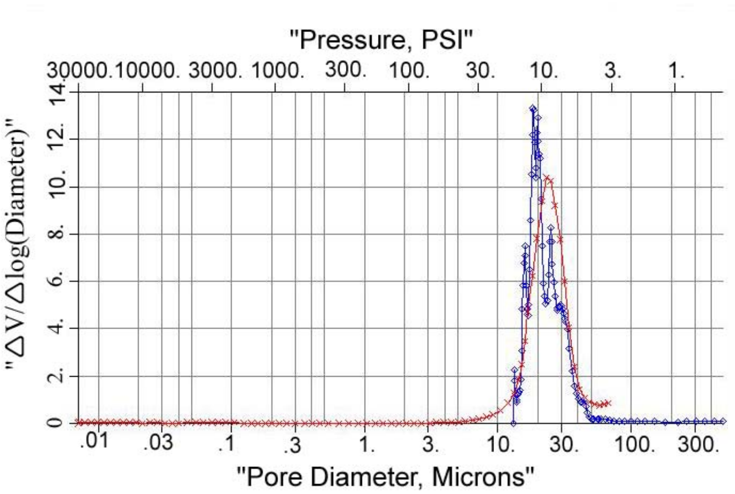

Figure. 4. Pore volume distribution measured by liquid extrusion porosimetry and mercury intrusion porosimetry.

Through pore surface area: The through pore surface area is computed using the following relation.

$$S = [1/(- \gamma \cos \theta)] \int p dV \qquad (4)$$

where S is the surface area. The computed surface area was 0.52m^2/g.

Liquid permeability: The flow rate of liquid was measured as a function of differential pressure. Typical results are shown in Figure 5. Liquid permeability is calculated from such data using the following relation.

$$F = k(A/\mu\, l)p \quad (5)$$

where k is liquid permeability, F is liquid flow rate, A is area of sample, μ is viscosity of liquid and *l* is sample thickness. The permeability of the sample computed using Equation 5, the slope of the plot in Figure 5, the thickness of sample, the area of the sample and the viscosity of water was 6.5 Darcies.

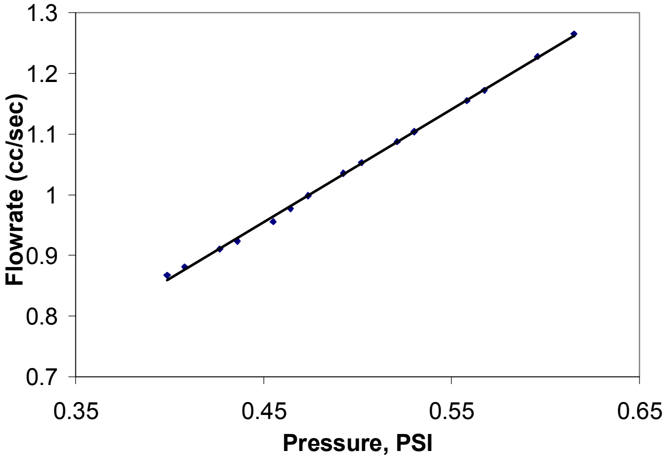

Figure 5. Variation of flow rate of liquid with differential pressure.

Comparison with Results of Mercury Intrusion Porosimetry

Pore volume: The pore volume measured by mercury intrusion porosimetry is shown in Figure 6. As expected, the pressured required for this technique is almost an order of magnitude higher than the pressure required for liquid extrusion porosimetry (Figure 3). The pore volume of 3.352cm^3/g measured by mercury intrusion porosimetry is the total pore volume of through pores and blind pores in the material. The volume of through pores measured by liquid extrusion porosimetry is 2.834cm^3/g. Hence, the blind pore volume is 0.518 cm^3/g. Thus, blind pores constitute 15.45% and the through pores constitute 84.55% of total pore volume in the material.

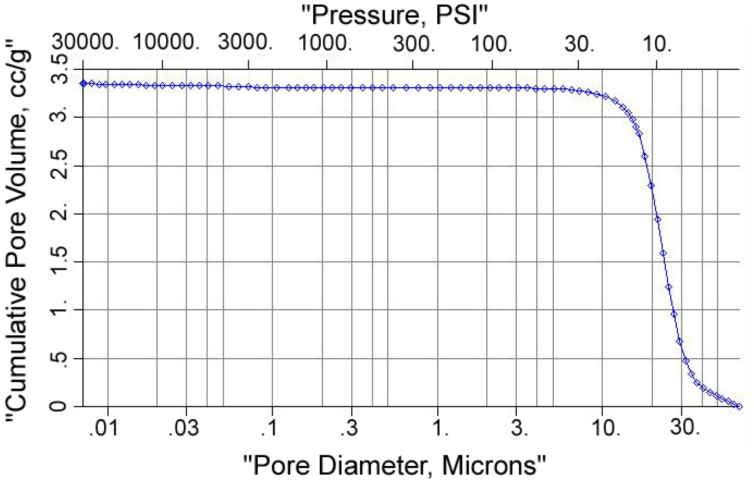

Figure 6. Cumulative pore volume measured by mercury intrusion porosimetry

Pore volume distribution: The pore volume distribution measured by mercury intrusion porosimetry is shown in Figure 4. The distributions by the two techniques are in excellent agreement with each other. The small increase in the median pore diameter detected by mercury intrusion porosimetry suggests that the blind pores have relatively wide parts. The mouths of such pores are likely to be wide.

Pore surface area: The surface area computed by mercury intrusion porosimetry is 9.85m^2/g. The liquid extrusion porosimetry yielded a surface area of only 0.52m^2/g for the through pores. The through pore volume of 0.518cm^3/g and median through pore diameter of 21.00µm yield the through pore surface area of 0.54m^2/g. The estimated value is in excellent agreement with the measured value of 0.52m^2/g. Therefore, the excess surface area of 9.33m^2/g detected by mercury intrusion porosimetry must be due to blind pores.

The contribution of blind pores to the surface area is large (94.7%), although the blind pore volume is only 15.45 %. It suggests that the blind pores must have narrow and long extensions of their wide mouths. The presence of small pores with very small pore volume could account for the surface area. For example, if only ten percent of blind pore volume is associated with the narrow parts of blind pores and the pore diameter of narrow parts is 0.02µm, the surface area would be 11.6m^2/g. This is close to the measured value of 9.33m^2/g. The sketch in Figure 7 illustrates the possible pore structure in the sample.

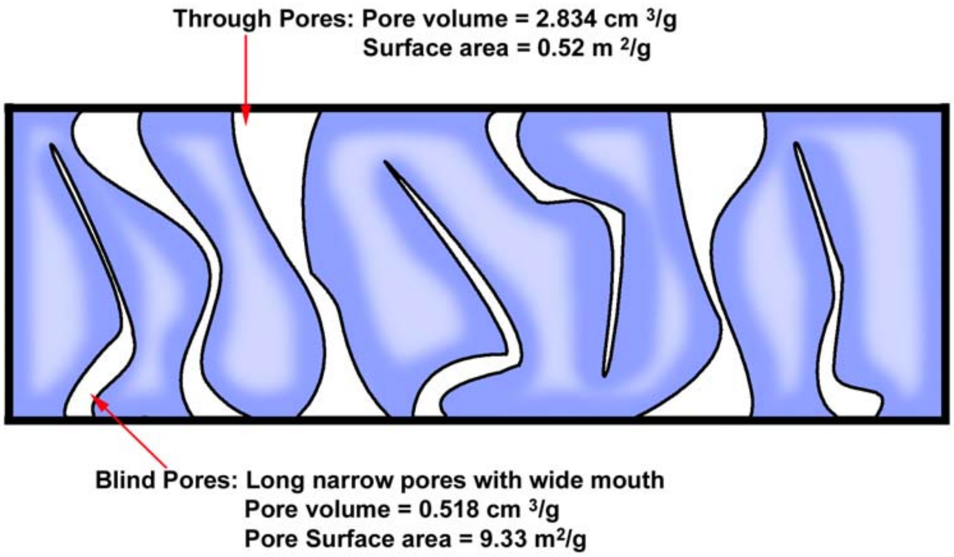

Figure 7. Suggested pore structure in the ceramic component.

Comparison of Techniques

Liquid extrusion porosimetry can measure a very unique combination of properties including permeability and characteristics of through pores. Mercury intrusion porosimetry cannot measure these characteristics, except in a very special case where the material is completely free from blind pores. Liquid extrusion porosimetry also has a number of operational advantages. The pressure required in this technique, is an order of magnitude less than that required for mercury intrusion porosimetry. Materials used in the extrusion technique are not toxic and are not harmful to health. Therefore, there is no cost related to sample disposal or safety regulations. The operation of the instrument is not involved. The results obtainable by the two techniques are compared in Table I.

Table I. Pore characteristics measured by the two techniques and their combination

Characteristic	Liquid Extrusion Porosimetry	Mercury Intrusion Porosimetry	Combination of Both Techniques
Through pore volume, cm^3/g	2.834	--	--
Volume of all pores, cm^3/g	--	3.352	--
Blind pore volume, cm^3/g	--	--	0.518
Median through pore diameter, µm	21.00	--	--
Median diameter of all pores, µm	--	22.86	--
Surface area of through pores, m^2/g	0.52	--	--
Surface area of all pores, m^2/g	--	9.85	--
Surface area of blind pores, m^2/g	--	--	9.33
Liquid permeability, Darcies	6.5	--	--

Summary and Conclusions

1. The novel technique, Liquid Extrusion Porosimetry has been described.
2. The technique was used to measure flow rate, volume of through pores (flow pores) and pore volume distribution.
3. No other technique, including Mercury intrusion Porosimetry is capable of measuring such combination of properties.
4. Pore volume and pore volume distributions measured by extrusion porosimetry and Mercury Intrusion Porosimetry were completely consistent with each other.
5. Liquid extrusion porosimeter does not use any harmful and toxic material. The pressure required is low. The procedure is simple, fast and inexpensive.
6. Combination of results obtained using the two techniques yields very interesting information on pore configuration.

References

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