

- Soil Mixtures." In *Highway Research Record 139*, HRB, National Research Council, Washington, D. C., 1966, pp. 1-14.
10. M. R. Thompson. "Split Tensile Strength of Lime Stabilized Soils." In *Highway Research Record 92*, HRB, National Research Council, Washington, D. C., 1965, pp. 69-80.
 11. T. E. Swanson and M. R. Thompson. "Flexural Fatigue Strength of Lime-Soil Mixtures." In *Highway Research Record 198*, HRB, National Research Council, Washington, D. C., 1967, pp. 9-18.
 12. P. G. Bhattacharya. *Static and Flexural Fatigue Strength of Lime-Laterite Soil—Plain and Fibre Reinforced*. Ph.D. thesis. Indian Institute of Technology, Kharagpur, India, July 1984.
 13. P. G. Bhattacharya and B. B. Pandey. "Study of Strength and Curing of Lime-Stabilized Soil—Plain and Fiber Reinforced." *Indian Roads Congress, Highway Research Board Bulletin 24*, 1984, pp. 1-26.
 14. P. G. Bhattacharya and B. B. Pandey. "Effect of Density on Strength and Modulus of Plain and Fiber Reinforced Lime-Laterite Soil Mixtures under Static and Repeated Load." Presented at Indian Geotechnical Conference, Calcutta, 1984.
 15. J. K. Mitchell and C. L. Monismith. "A Thickness Design Procedure for Pavements with Cement Stabilized Bases and Thin Asphalt Surfacing." *Proc., 4th International Conference on Structural Design of Asphalt Pavements*, University of Michigan, Ann Arbor, 1977.
 16. D. Croney. *The Design and Performance of Road Pavements*. Her Majesty's Stationery Office, London, 1977.
 17. L. W. Locket and R. K. Moore. "Lime-Soil Mixture Design Consideration for Soils of Southeastern United States." In *Transportation Research Record 839*, TRB, National Research Council, Washington, D. C., 1982, pp. 20-25.

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Experimental Aspects of Mercury Intrusion Porosimetry

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Several frequently ignored aspects of mercury intrusion porosimetry are discussed. The importance of knowing the correct contact angle between the mercury and the solid is emphasized. It is also suggested that mercury intrusion be considered in some instances when a specific surface measurement is desired. Also, a method for handling inhomogeneous samples is discussed. Finally, a possibly instructive use for the hysteresis found on depressurization is explored.

Mercury intrusion has become the predominant experimental technique for determining pore-size distributions. This is because modern instrumentation allows one to measure rapidly pores with sizes ranging over about six orders of magnitude. Much of the experimental technique and data reduction has become routine, and ASTM standard methods are beginning to appear (ASTM D 4284-83 and D 4404-84).

Nevertheless, certain experimental aspects have not received the attention that the author believes they deserve. It is the intent of this paper to discuss several of these aspects. It is assumed that the reader is familiar with the fundamentals

behind the phenomenon of mercury intrusion and with the basis of the experimental technique. A general reference for experimental technique is *Surface and Colloid Science* (1, Vol. 13, Ch. 6).

CORRECT CONTACT ANGLE

It is necessary to know the applicable contact angle in order to accurately convert the pressures that are recorded during an intrusion experiment into their corresponding pore sizes. In some cases, the exact value of this angle is not particularly important. If tests are being conducted merely to determine whether or not a piece of porous material has the same pore structure as a companion piece of the same material, any angle will serve. Indeed, under such circumstances, one can make the comparison by using the pressure-intrusion data without bothering to convert the pressures into pore sizes.

However, when the aim is to correlate pore sizes with some other property of a material, a wrong impression may be obtained if the pore sizes are incorrectly calculated. Another case in which accurate angles are needed is in the comparison of the pore structures of different materials. This is because the contact angle is a function of the surface properties of both the

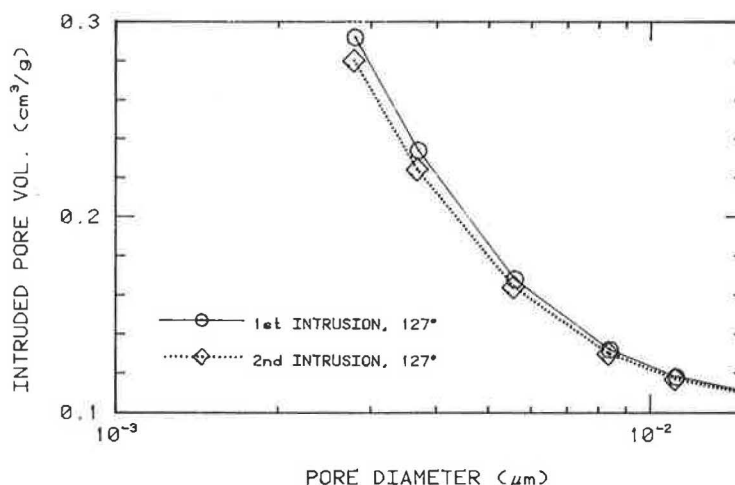


FIGURE 1 Pore-size distributions of alumina plotted with the same contact angle.

mercury and the porous solid. These latter properties can be expected to vary between different materials.

An example of a wrong impression is given in Figure 1. It shows two pore-size distributions of a sample of porous alumina. Only the distributions of the smaller pores are shown, to emphasize the point being made. The solid line is the distribution found during the first intrusion of a virgin sample. The dotted line is the distribution found on a second intrusion after removal of the mercury by distillation. Both are plotted using a contact angle of 127 degrees. This is the angle that was found to be applicable for the virgin alumina.

The obvious conclusion from Figure 1 is that the act of intruding the sample has caused some crushing and that the pore volume has been reduced. This appears to be especially true in the smallest pore size ranges where the pressure is the greatest, an apparently logical finding. However, the act of distilling the mercury from the sample has left its surface somewhat altered. A direct measurement of the applicable angle showed that it had changed to 131 degrees.

This change of 4 degrees may appear small at first glance, but it is the cosine of this angle that is used in the conversion of

pressure to size. The cosines of the two angles differ by about 9 percent, and thus there is a 9 percent error in the sizes of the pores depicted by the dotted line in Figure 1. When the correct contact angle is used for each set of data, the result is as shown in Figure 2.

The conclusions from Figure 2 are different; there has been no crushing of the sample during the initial intrusion, and its pore structure has remained unchanged. This is an example of why applicable contact angles must be determined for critical research work. Measuring contact angles is a laborious operation (2), but it is necessary if wrong conclusions are to be avoided in research.

MEASUREMENT OF SURFACE AREA

A number of years ago, Rootare and Prenzlow (3) derived a method for obtaining a measure of the surface area of a sample directly from the curve of pressure versus intruded volume of an intrusion experiment. Basically, the technique yields the surface area of a sample by finding the amount of work (the

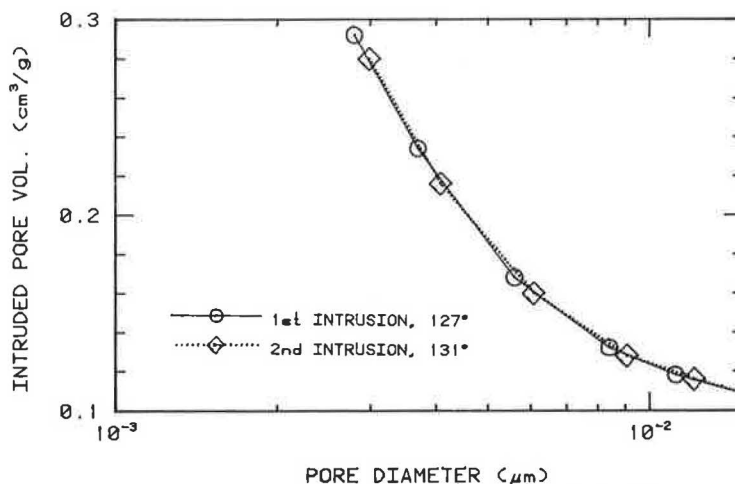


FIGURE 2 Pore-size distribution of alumina plotted with different, correct contact angles.

area under the curve of pressure versus volume) needed to cover the surface with mercury. This technique does not appear to be widely used. However, it has certain unique advantages over the more traditional vapor sorption technique and deserves more attention.

The traditional vapor sorption technique becomes experimentally difficult when the sample has a small surface area because so little vapor is adsorbed. It is precisely this class of samples for which the intrusion procedure is ideally suited, and experimenters might consider performing an intrusion experiment solely to obtain a measure of surface area. For example, several results for some samples of fly ash are as follows:

Sample	Area	
	By Intrusion (m ² /g)	By Sorption (m ² /g)
NIP 1A	1.6	1.7
NIP 2	2.3	2.1
NIP 1	4.2	4.1

Generally one is not interested in the distribution of the interparticle pores in a collection of fly-ash particles. However, mercury intrusion proved to be a rapid and accurate method of obtaining the surface area of the samples discussed here. The foregoing data indicate that the intrusion procedure gives results comparable to those obtained by vapor sorption, and these were obtained in about 1 percent of the time required for sorption.

One strong note of caution about the use of this intrusion technique: if insufficient pressure is available to intrude all the pore space and cover all the surface, this method will return an erroneously low measure of the surface area. On the other hand, if higher pressures cause a crushing of sealed pores, this method will yield an erroneously high measure. Usually, when these complications are not present, the curve of pressure versus intrusion will flatten out, and no further intrusion will be recorded for the higher pressures. Thus, if the intrusion curve is still rising at the highest pressures, the method is probably not applicable. Figure 3 demonstrates this important difference with two distributions. One shows continued intrusion, and the other shows that intrusion has stopped. Fortunately, for many

materials with small surface areas such as coarse-grained soils, the intrusion curves do flatten out, and the method has considerable merit.

HANDLING HETEROGENEOUS SAMPLES

Most porosimeters can only accept samples with a bulk volume of a few cubic centimeters. This does not present a sampling problem as long as the material has a pore structure that is homogeneous within this volume. However, many construction materials are not this uniform. One obvious strategy is to perform a number of tests and to combine the results. This is the equivalent of performing a single test on a much larger sample, but it requires extensive testing.

An alternative approach is suggested here that, under the right circumstances, can be used to greatly reduce the number of tests. The procedure envisions a large sample, such as a piece of rock or brick, from which subsamples with a volume of a few cubic centimeters possess substantially different pore volumes. This is what is meant here by a heterogeneous pore structure.

The first step is to crush the material and to separate a certain size fraction, that is, material passing the No. 4 sieve and retained on the No. 8. This material is then reduced with a sample splitter until one has a sample with sufficiently few grains to permit testing. This technique allows one to test more randomly selected pieces simultaneously, which has the effect of smoothing out variations in pore structure and giving one a reasonable chance of testing a homogeneous sample.

One can assess the efficacy of this procedure by looking at the coefficient of variation of the total intruded pore volumes from repeat tests with different sizes of crushed pieces. Data for two materials are as follows:

Material	Particle Size	Coefficient of Variation (%)
Limestone	1/2-3/8 in.	28.9
Limestone	No. 4-No. 8 sieve	4.0
Masonry brick	3/8 in.-No. 4 sieve	6.8
Masonry brick	No. 4-No. 8 sieve	3.0

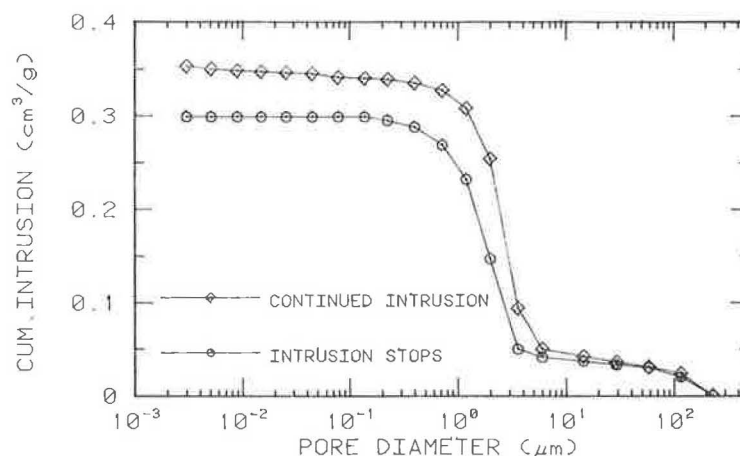


FIGURE 3 Pore-size distributions showing continuing and completed intrusions.

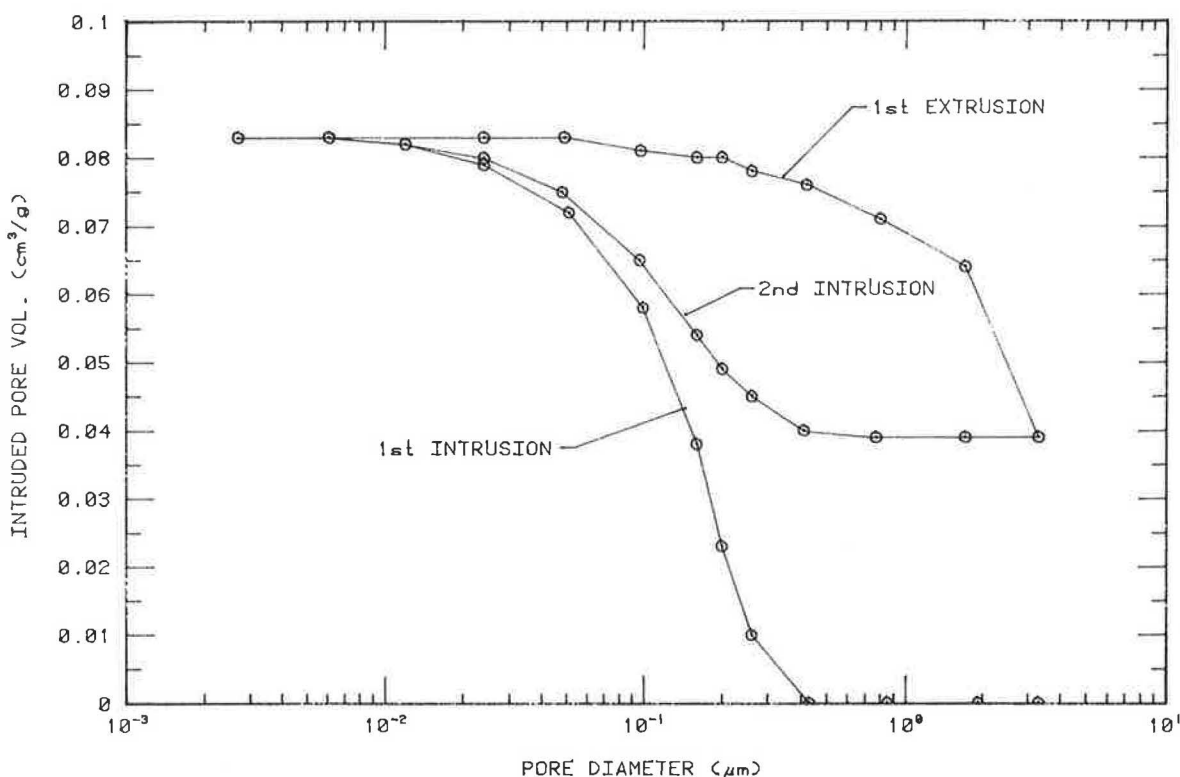


FIGURE 4 Hysteresis during mercury intrusion and extrusion.

These data indicate that scatter in results can be significantly reduced by this procedure. Thus, the number of tests required to be confident in one's results is reduced also.

There is one difficulty with this technique. The collection of smaller particles inside the porosimeter generates some inter-particle porosity that is not present in the larger mass of the parent sample. As long as reasonably large particles are tested, most of this false porosity will lie in the larger pore-size range. One must subtract this extra porosity before using the results. However, if the parent material has innate porosity in this same size range, this correction cannot be made. Thus, one needs to do a certain amount of testing with large, single pieces of the material to ensure that one is justified in using this technique and to select the best crushed size fraction for the material in question.

HYSTERESIS IN PORE-SIZE DISTRIBUTIONS

The pore-size distributions derived from mercury intrusion and mercury extrusion are different for virtually all porous materials. Typically, one-third to two-thirds of the intruded mercury does not spontaneously exit the pore structure on depressurization. Lowell and Shields (4) have examined this hysteresis in a new way. For the distributions in Figure 4 (determined by the author for a limestone), the first intrusion and the first extrusion pore-size distributions are seen to be widely different. On repressurization (the second intrusion curve of Figure 4), the intruded pore volume returns to its previous maximum. Subsequent depressurization was found to retrace the first extrusion curve, and repressurization was found to retrace the second intrusion curve. Thus the total hysteresis, starting from the first

intrusion, consists of two parts: an irreversible and a reversible portion.

Whatever the reasons for the irreversible hysteresis, Lowell and Shields found one consistent reason for the reversible part: the advancing and receding contact angles for mercury are different. Receding contact angles are typically smaller than advancing ones, and Lowell and Shields found that the reversible hysteresis loop could be completely eliminated by the selection of an appropriately smaller angle for the extrusion leg of the cycle. Figure 4 was plotted by using only the appropriate advancing contact angle of 125 degrees. However, if the extrusion curve had been plotted with a receding angle of 93.5 degrees, it would coincide with the second intrusion curve. In other words, the second intrusion curve represents both second and subsequent intrusions and subsequent extrusions, if the appropriate contact angles are invoked.

This means that the second intrusion curve is the pore-size distribution of that portion of the total pore structure that can be reversibly intruded. If this reversible distribution is subtracted from the total pore-size distribution, one obtains the irreversible pore-size distribution as well. Figure 5 shows the results of separating these two distributions from the total pore-size distribution shown in Figure 4.

The two distributions in Figure 5 are not the same. One has significantly more small pores, and the other has a greater pore volume in the size range centered around 0.1 μm. When the same sort of subdivision is performed on other distributions, the resulting distributions are frequently even more dissimilar.

It may be that one or the other better correlates with and explains other properties of a material than does the total pore-size distribution. For example, one might postulate that the reversible pore structure represents those pores that are more

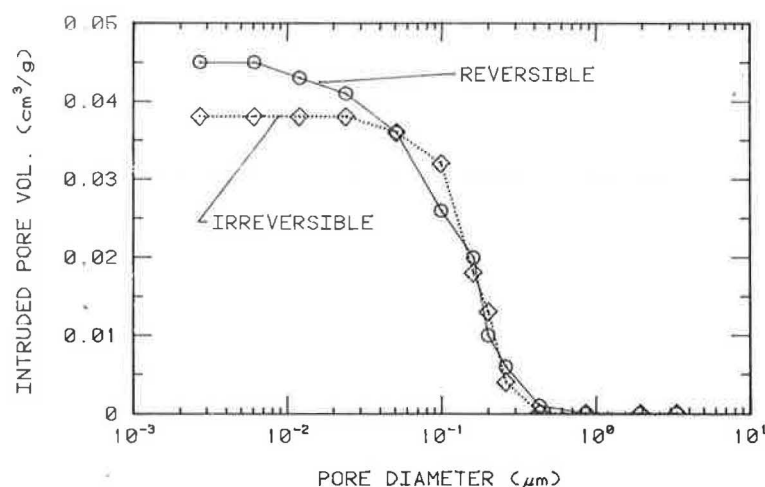


FIGURE 5 Reversible and irreversible parts of a pore-size distribution.

directly connected and accessible. It may be only this part of the pore structure that dictates the permeability of the material and not the total pore-size distribution. This approach has not been attempted. However, it appears to be a potentially fruitful extension of the technique that may lead to more informative results.

CONCLUSION

Mercury intrusion porosimetry is now a well-developed experimental procedure. However, there are applications for it that have not been much used, and there are variations on the standard uses that appear promising for obtaining additional information. It is hoped that this paper will suggest new avenues to researchers.

REFERENCES

1. *Surface and Colloid Science* (E. Matijevic and R. J. Good, eds.), Plenum Press, New York, 1984.
2. D. N. Winslow and S. Diamond. *ASTM Journal of Metals*, Vol. 5, 1970, p. 5.
3. H. M. Rootare and C. F. Prenzlow. *Journal of Physical Chemistry*, Vol. 71, 1967, p. 2733.
4. S. Lowell and J. E. Shields. *Journal of Colloid and Interface Science*, Vol. 80, 1981, p. 192.

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