

PORE SIZE DISTRIBUTIONS IN CLAYS

SIDNEY DIAMOND

Purdue University, Lafayette, Indiana 47907

(Received 11 August 1969)

Abstract—A knowledge of the distribution of pore sizes in clay and soil bodies is a useful element in the microstructural characterization of such materials. Pore-size distributions and total porosity of a number of reference clays, naturally-occurring subsoils, and commercial clay samples prepared in various ways were determined by mercury porosimetry. The range of equivalent pore diameter explored covered almost five orders of magnitude, from several hundred microns down to approximately 150 Å. The method and its assumptions are critically evaluated, and measurements of the contact angle of mercury on clays yield values of 139° for montmorillonite and 147° for kaolinite and illite clays. The extent of shrinkage on oven-drying prior to mercury intrusion is assessed in each case and found to vary from insignificant to as much as 30 per cent of the pore space, depending on microstructural state and degree of initial saturation. The development of techniques for water removal which do not involve change in pore structure is explored. Some preliminary results for structurally weak saturated clays suggest that critical-region drying and perhaps freeze-drying procedures may be practical.

INTRODUCTION

A COMPLETE physical description of the state of a clay soil or an experimental clay mass is often of considerable interest. Usually the information available is confined to measurements of gross parameters, such as moisture content, bulk density, total porosity, etc. Less frequently additional descriptors such as particle-size distribution, surface area, and information on mutual orientation of particles is supplied.

In many instances knowledge of at least one additional parameter, the mathematical distribution of pore sizes in the mass, may assist in interpreting the behavior of the material. Changes in the pore-size distribution arising from mechanical loading, remodeling, chemical treatment, plant root growth, freezing and thawing, or other influences often need to be taken into account in interpreting experimental results. It is the purpose of this paper to call attention to the fact that direct measurements of this property may readily be performed, to illustrate the results obtained for various clay and soil materials, and to discuss the limitations of the technique employed.

There are two major approaches currently available for the determination of pore size distributions in porous solids, viz.: forced intrusion of a non-wetting fluid (usually mercury) under pressure, and the "capillary condensation method," which involves interpretation of adsorption or desorption isotherms to calculate that portion of the sorption that is due to capillary condensation. The latter method is much more difficult experi-

mentally and suffers from the limitation that the maximum pore diameter that can be tallied is of the order of 1000 Å, much smaller than many of the pores present in clays. In consequence, no further discussion is made of the capillary condensation approach and the remainder of this paper is concerned with mercury intrusion measurements.

THE METHOD OF MERCURY INTRUSION

The basis of the mercury intrusion method, as conceived originally by Washburn (1921) and subsequently applied by Ritter and Drake (1945), Winslow and Shapiro (1959) and others, rests on the simple physical principle that a non-wetting fluid, i.e. one whose contact angle is greater than 90° for a particular solid, will not spontaneously intrude the pores of that solid but will do so if sufficient pressure is applied. The pressure required depends on the contact angle, the pore shape, and the surface tension of the liquid. For pores of cylindrical shape the relationship between pressure and the minimum pore diameter which may be intruded was given by Washburn as:

$$P = -4\gamma \cos \theta / d \quad (1)$$

where P is the required pressure
 γ is the surface tension of the liquid
 θ is the contact angle
 d is the diameter of the pore.

Since most porous media contain pores of irregular and widely-varying shape, pores that are

intruded under a given pressure are referred to as having an "equivalent" cylindrical diameter as calculated from Equation (1).

Experimentally, the method consists of the following steps: one applies an increment of pressure to a suitable experimental apparatus in which mercury (or other non-wetting liquid) is permitted to intrude the pores of a sample; one measures the volume intruded when the liquid ceases to flow; and then one repeats the process under successively higher pressures to the limit of the apparatus. The volume of mercury intruded in a given step is taken as the total volume of pores with equivalent diameters smaller than that corresponding to the preceding pressure and larger than that corresponding to the pressure causing the flow. By adding the results of all of the steps a cumulative volume distribution with respect to pore diameters is built up.

Several inherent characteristics of the method should be noted:

- (a) The pores must be empty of water or any other fluid at the start of the experiment.
- (b) Completely isolated pores inaccessible to the exterior of the sample cannot be measured.
- (c) Pores accessible only through entryways of smaller diameter will not be intruded until sufficient pressure is applied to intrude the entryways or "necks"; hence, all of the volume of such pores will be allocated to the diameter class of the most restricted part of the entryway.
- (d) Even if all of the pore space is accessible to the outside, the entire volume of pores of a given sample may not be measured, depending on whether the instrument has sufficient pressuring capacity to intrude the finest pores present.

SPECIAL SAMPLE PREPARATION PROBLEMS WITH CLAYS

The size of sample that can be employed is limited by the capacity of the intrusion readout system employed. In the usual forms of mercury intrusion apparatus this capacity is of the order of several tenths of a cubic centimeter, restricting sample sizes to the order of 1 g.

For most porous substances, the critical requirement that the pores be empty at the start normally is met by oven drying the sample, followed by evacuation to comparatively low pressures. While the effects of oven drying and evacuation are of little consequence for most materials, partly or completely saturated clay (or soil) bodies may

shrink appreciably on drying, decreasing the total porosity by an often significant amount. Details of the shrinkage process depend on the initial moisture content and degree of saturation, the microstructure of the clay, and probably the details of the drying process itself (Yong and Warkentin, 1966, pp. 151-159). The particle rearrangements involved not only reduce the total porosity but inevitably change the distribution of pore sizes as well, to a degree that cannot be completely predicted. The effect of the foregoing is that the pore-size distribution obtained from a clay mass after oven drying does not completely reflect the distribution previously existing in the partly or completely saturated sample of interest. Methods of removing the water in such a way as to avoid bulk shrinkage and particle rearrangement are currently under study and certain results already obtained are presented later in this report.

The bulk of the work reported here has been done on oven-dried samples. In cases where a definite reference state exists, an effort has been made to assess the shrinkage involved in oven-drying, and the consequent changes in pore size distribution that may have taken place. It should be noted that the range of pore sizes covered extends over five orders of magnitude; in consequence small shifts in the experimental pore size distribution function associated with minor shrinkage effects will likely not affect the general import of the data.

EXPERIMENTAL DETAILS

The pressuring equipment used in this study was a modified Aminco-Winslow porosimeter (American Instrument Co., Silver Spring, Md.) with a pressuring capacity of 15,000 psi and a mechanical sensing device capable of registering intrusion of mercury in increments of 0.0001 ml. The filling device supplied with this equipment was removed and a separate filling device of advanced design* was used for the initial mercury filling and for measurement of intrusion at pressures less than 1 atm. This device, in which the dilatometer ("penetrometer") is filled while in a horizontal position, permits filling of the dilatometer under essentially zero head of mercury. Its use extends the practical upper limit of pore diameter that can be measured to approximately 800 μ , a feature of some importance with some clays and many soils.

Standard dilatometers of approximately 6 ml capacity and 1.3 mm bore diameter were used, as

*U.S. Pat. No. 3,438,245 awarded to Prado Laboratories, Cleveland, Ohio, April 15, 1969.

illustrated in Fig. 1. The sequence of operations was as follows:

- (1) The sample, of appropriate size and state of dryness, was weighed analytically and placed in the dilatometer, which was then assembled, weighed, and inserted into the filling device. The entire system was then evacuated to a residual pressure of approximately 10μ Hg, as measured with a McLeod gauge.
- (2) Mercury was admitted to the filling device to a level just commensurate with the top of the borehole in the stem of the dilatometer. The pressure was increased to approximately 10 mm Hg by means of a bleeder valve connecting the evacuated system to the atmosphere, and the space surrounding the sample in the dilatometer allowed to fill with mercury. Pressures in this range were measured with a mercury manometer.
- (3) The residual mercury in the filling device was drained, and the position on the stem of the dilatometer at which the mercury column broke off was recorded.
- (4) The atmosphere bleeder valve was again opened and the pressure increased by an appropriate increment, forcing mercury into the largest accessible pores in the sample. After the cessation of flow, the new position of the mercury meniscus along the calibrated stem of the dilatometer was recorded, the difference in position indicating the amount of mercury intruded into the sample. The precision of reading the position of the meniscus visually was probably not much better than 0.0005 ml.
- (5) This process was repeated a number of times until atmospheric pressure was reached. Subsequently, the dilatometer was removed from the filling device, weighed again to determine the amount of mercury held, and transferred to the hydraulic pressuring chamber of the porosimeter. In this chamber pressure is generated by an electrically-driven hydraulic pump, and transmitted to the chamber using ethanol as the working fluid. Pressuring was continued in increments between 15 and 15,000 psi, pressure being read by Bourdon-tube gauges and the amount of intrusion recorded digitally by a mechanical readout device in units of 0.0001 ml. Twenty to thirty increments of pressure were recorded for the typical determination.

From the data secured it was possible to calculate cumulative pore size distribution on a weight,

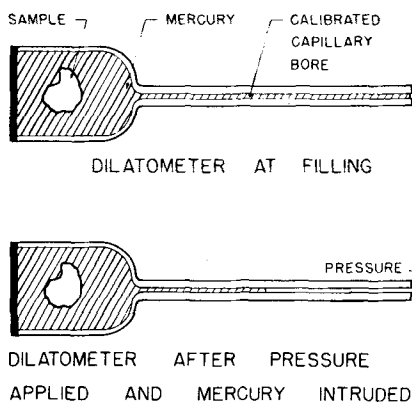


Fig. 1. Schematic view of dilatometer after filling, and after pressure has been applied and mercury has intruded into the sample.

volume, or percentage of total pore space basis; sample bulk volume; and, based on an assumed specific gravity for the clay, the total porosity in terms of pore volume in cm^3 per g of clay. It was also possible to employ the penetrometer to measure the bulk density of a corresponding undried sample and thus calculate the total porosity in the undried condition.

In the conduct of the mercury intrusion experiment and in the resulting calculation of the pore size distribution curve several cautions and corrections need to be observed:

- (a) The time required for equilibration varies with the nature of the pore system and is not uniform from step to step within a given run. Care must be taken to insure completion of the intrusion process at a given pressure before the next pressure increment is applied.
- (b) In the initial evacuation step a small but finite residual amount of air is trapped within the penetrometer. A Boyle's Law correction for the decreasing volume of this trapped air at each increment of increasing pressure is appropriate. This is numerically important only at pressures below one atmosphere.
- (c) A further correction is required for the effective compressibility of the mercury in the penetrometer for pressures higher than approximately 100 psi. The amount of the correction may be ascertained by noting the apparent intrusion under a pressure cycle of a penetrometer filled entirely with mercury, without a sample being present. The correction required is significantly less than that which would be calculated from the bulk compressibility of mercury since the applied

pressure also acts to reduce the internal volume of the glass penetrometer. For a 6.1 cm³ dilatometer, calculations based on the compressibility of mercury would predict a correction of 0.0214 cm³ at 15,000 psi; the experimental value recorded at this pressure is less than one-third of this, 0.0066 cm³.

SURFACE TENSION AND CONTACT ANGLE VALUES

The equation used in calculating the diameter class corresponding to the pressure applied (Equation (1)) requires a knowledge of both the surface tension of the liquid and its contact angle on the solid being intruded.

There are a number of determinations of the surface tension of mercury in the literature. The value of 484 dynes/cm at 25°C (Kemball, 1946, Nicholas *et al.*, 1961) was selected as the best value available and used throughout. Every effort was made to insure that the mercury used in each experiment was scrupulously clean, and mercury coming into contact with a sample was discarded and replaced after each run.

The question of an appropriate contact angle is a little more complicated. Many workers in mercury porosimetry apparently have selected a single value for the contact angle of mercury out of the comparatively few measurements available in the literature, and have applied this value to all substances tested. The usual values so employed are 130° (Winslow and Shapiro, 1959) or 140° (Ritter and Drake, 1945).

There is an apparent absence of measurements of the contact angle of mercury on clays in the literature. In view of this, measurements of this parameter were undertaken by the author using the sessile drop method whose use is described (for spreading coefficient measurements) by Padday (1953). The method consists of measuring the heights of sessile drops of the liquid on a horizontal surface of the solid to be studied as a function of drop weight or size. There is a maximum drop height that can be supported regardless of increasing drop size. This is related to the contact angle by Equation (2), given in essence by Adam (1941).

$$\cos \theta = -\frac{gDh^2}{2\gamma} + 1 \quad (2)$$

where θ is the contact angle

g is the acceleration due to gravity

D is the density of the liquid

h is the maximum height of the sessile drop

γ is the surface tension of the liquid.

Several preliminary measurements of contact angles undertaken to check the technique yielded values of 137° for mercury on clean glass plates and 112° for water on paraffin-coated glass plates, both values being in accord with previously-published determinations (Adamson, 1967; Padday, 1953). Determinations were then carried out on glass plates coated with uniform layers of clay which were deposited from dilute suspension, air-dried, and then oven-dried prior to examination. Results for kaolinite and illite samples were within a degree of an average value of 147°, while those for three different montmorillonites (a sodium-calcium bentonite, a highly organic montmorillonite soil clay, and an iron-rich montmorillonite soil clay) were all within a degree of an average value of 139°. A representative determination, for mercury on a Georgia kaolinite, is given in Fig. 2. In the calculations reported in this paper the contact angle value employed was 139° for montmorillonite clay and 147° for all other clay mineral types.

PORE SIZE DISTRIBUTION CURVES

Data presentation and reproducibility

In this paper the experimental pore size distribution data are presented in the form of cumulative pore diameter distribution curves, the pore volume parameter being expressed as cm³ of pore space per gram of oven-dried clay. The data are culminated from largest pore diameter measured (on the right-hand side of the figure) to the smallest diameter limit set by the pressuring capacity of the instrument. In presenting pore size distribution curves over limited size ranges, some authors prefer to present the derivative distribution function ($d(\text{vol.})/d(\text{diam.})$) rather than the cumulative function, but the derivative function is severely distorted for data covering several orders of magnitude of pore sizes. Further, the cumulative or integral function used here has the distinct advantage that the fraction of pore space between any arbitrary bounds of pore size can be assessed at a glance.

Reference clay mineral samples

A great deal of information has been published on various characteristics of the reference clay mineral standards distributed under the auspices of the American Petroleum Institute's Project 49 (Preliminary Reports, Reference Clay Minerals, A.P.I. Research Project 49; Columbia University, New York, January 1951). While samples of the original Project 49 set were not available for this project, pore-size distribution data were secured for samples collected at the same sites by Holmes and

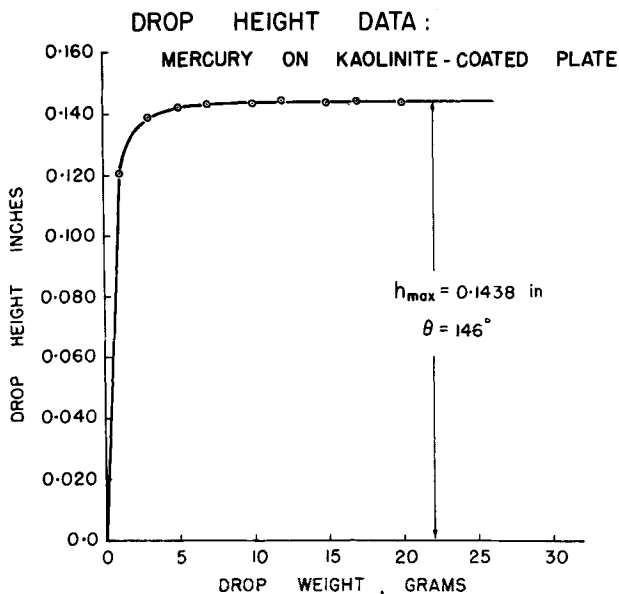


Fig. 2. Drop height data for mercury on kaolinite-coated glass plate.

distributed by Ward's Natural Science Establishment.

These clay samples are supplied as partly-ground and mixed pieces of size ranging up to an inch or more. The specimens employed in the pore-size distribution work were selected from the larger fragments and cut to appropriate size using a wood chisel. The samples were all sensibly air dry as supplied, although the initial hygroscopic moisture ranged up to about 19 per cent.

The reproducibility of the pore-size distribution curve was found to depend largely on the uniformity of the specimen material with reference to the very small sample sizes that could normally be run. Where the clays concerned are microscopically homogeneous (such as the reference kaolinite from Macon, Georgia) or where an artificial sample has been prepared in such a way that homogeneity on a small scale exists (such as the compacted grunsite samples), replicate runs trace the identical pore size distribution curve to a high degree of precision, as indicated in Fig. 3. Where the clays or soils are not homogeneous on a small scale, such as the reference halloysite from Bedford, Indiana or the natural subsoil samples from Indiana, replicates are not identical but naturally vary with the characteristics of the individual small specimen tested. All of the data presented in this report are individual runs which either are identical to other replicates or are judged most representative of a set of differing replicates.

Selected samples were oven dried overnight and the pore-size distributions obtained, together with relevant information on shrinkage of the pore space accompanying the oven-drying process. Pertinent information on these samples is summarized in Table 1 and the pore-size distribution curves are given in Fig. 4 and Fig. 5. The numerical data of Table 1 representing the average values cited for total penetration of mercury into a particular material may be slightly different from that shown in the corresponding curve of Fig. 4.

Figure 4(a), for the Fithian illite, is an illustration of an extremely "tight" microstructure. Total penetration of mercury into the samples is low (less than 0.03 cm³/g); this is less than one-third of the comparatively small volume of pores calculated to be present after oven drying. Since the "as-supplied" moisture content is so low, the shrinkage on oven drying was negligible. The pore space that has been intruded is distributed over the full range of pore sizes explored, the only noteworthy feature of the distribution curve being the upturn in pore volume for diameters less than 300 Å. It seems likely that most of the residual pore space not assayed is in pores less than 160 Å in diameter. The fineness of the pores is a consequence of both small particle size (external surface areas of 70-80 m²/g are usually observed) and of the geological consolidation processes undergone by this clay.

Figures 4(b) and 4(c) give typical curves for the Clay Spur montmorillonite and the Garfield nontronite samples, respectively. Both clays suffer

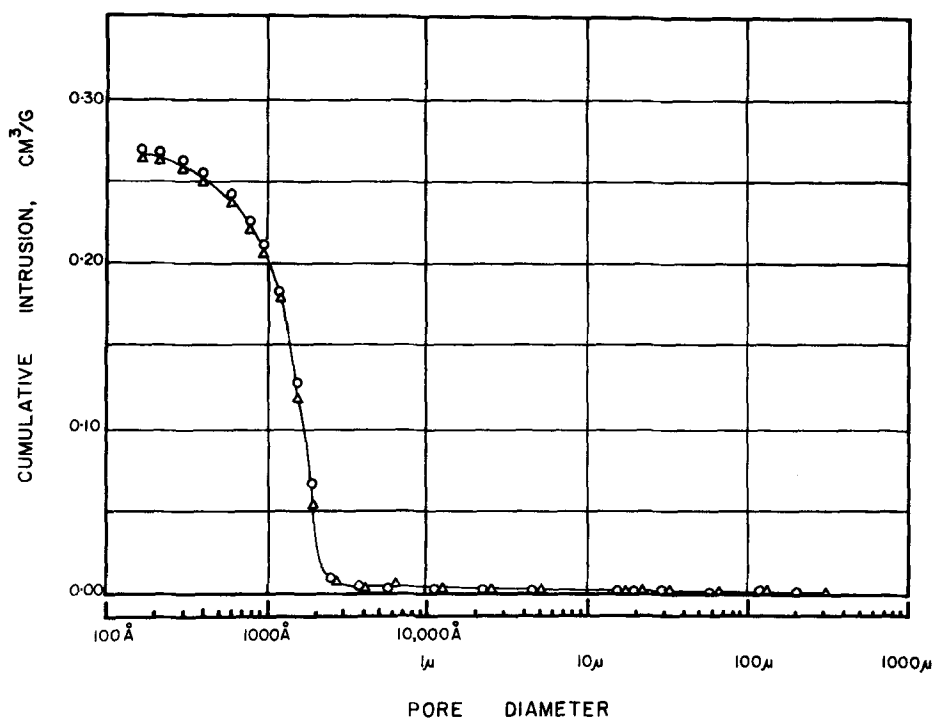


Fig. 3. Replicate pore-size distribution determinations for Macon, Georgia kaolinite.

Table 1. Porosity and related characteristics of selected reference clays

API No.	Clay mineral type	Location	Total porosity in "as supplied" condition* (cm ³ /g)	Moisture content "as supplied" (%)	Total porosity after oven drying† (cm ³ /g)	Porosity intruded by mercury (cm ³ /g)
H-35	illite	Fithian, Ill.	—	3.5	0.09 ₈	0.02 ₇
H-26	montmorillonite	Clay Spur, Wyo.	0.17 ₂	13.1	0.14 ₅	0.11 ₃
H-33a	nontronite	Garfield, Wyo.	0.25 ₅	19.0	0.21 ₈	0.16 ₄
H-4	kaolinite	Macon, Ga.	0.27 ₈	1.3	0.27 ₈	0.26 ₇
H-22	halloysite	Bedford, Ind.	0.25	13.4	0.34	0.27 ₂

*Calculated from bulk density of undried samples as measured by mercury displacement using assumed specific gravity values for the clay mineral types as follows: illite—2.89; montmorillonite—2.80; nontronite—3.10; kaolinite—2.65; halloysite—2.56.

†Calculated from bulk density of oven-dried samples as measured in the porosimeter and the assumed specific gravity values.

a slight loss in total pore space on oven drying, as indicated in Table 1, but the losses (less than 0.03 and 0.04 cm³/g, respectively), are much less than the volumes of hygroscopic moisture removed (13 and 19 per cent by weight, respectively). For the montmorillonite, it was determined that the X-ray basal spacing dropped from 12.6 Å as received (indicative of a statistical monolayer of interlayer water) to 9.7 Å after oven drying, indicative of a loss of volume within "particles"

of 25 per cent; yet this loss was not translated into any significant loss of pore space within the microstructure of the aggregate of particles constituting the sample.

For both montmorillonite and nontronite, about three-quarters of the total pore space after oven drying could be intruded by mercury at the pressure range available, i.e. existed in accessible pores larger in equivalent diameter than about 140 Å. For the montmorillonite, Fig. 4(b) shows compara-

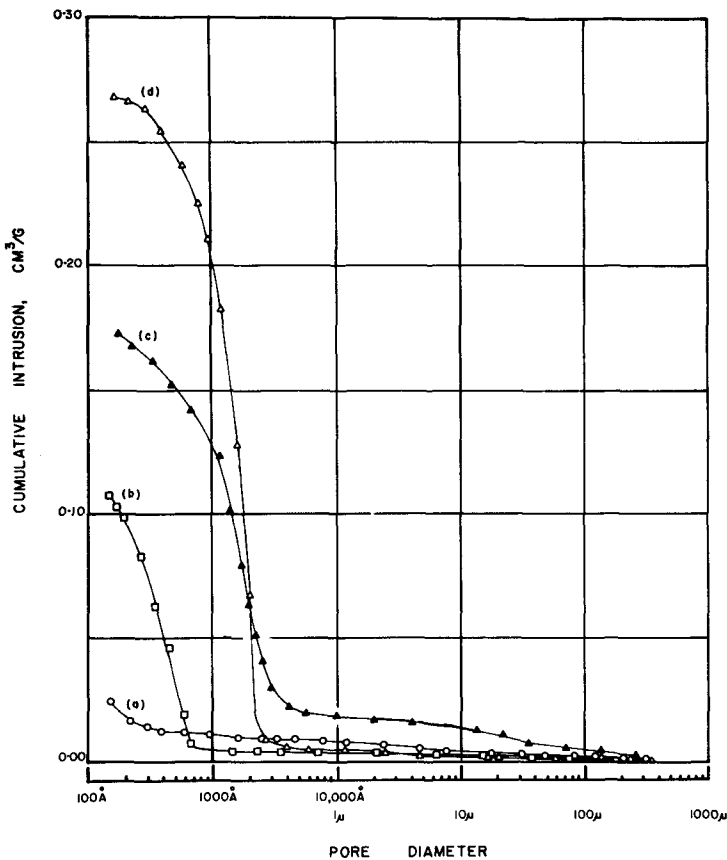


Fig. 4. Pore-size distribution curves for reference clay samples: (a) Fithian illite; (b) Clay Spur montmorillonite; (c) Garfield nontronite; (d) Macon kaolinite.

tively little intrusion until pressure sufficient to intrude pores of 650 Å diameter is reached; well over 90 per cent of the mercury intrusion recorded occurs in pores of diameters between this value and the 40 Å lower limit of assay set by the pressuring capacity of the instrument and the contact angle. Judging from the strong upward trend of the curve at the lower limit of assay, most of the residual unintruded pore space would be expected to lie in diameter classes just beyond the limit. The nontronite sample appears to be considerably more open; the intrusion curve "breaks" at about 5000 Å rather than 650 Å, and the intrusion takes place over a considerably greater range of pore diameters. Again, most of the residual undetected pore space probably occurs as pores just beyond the 140 Å lower limit of assay.

Figure 4(d), the curve for Macon kaolinite, shows that essentially all of the pore space present was intruded by mercury. It is apparent that the bulk

of the pores are in diameter classes within a narrow range of about 300 Å to about 2000 Å, or else are accessible only through pores of such equivalent diameters. It is certain that virtually no pores finer than about 300 Å in equivalent diameter are present, in contrast to the results for the 2:1 phyllosilicates which suggest significant porosity in very fine pores.

Figure 5 shows results for the Bedford halloysite sample, which reflect a phenomenon somewhat at variance with that recorded for the other clays. In contrast to the usual reduction in pore space resulting from oven drying, the data in Table 1 show that this clay expanded significantly on oven drying; pore space increased from about 0.25 to about 0.34 cm³/g, both expressed on an oven-dry basis. Figure 5(b) is the pore-size distribution curve generated in the normal manner after oven drying; Fig. 5(a) is the apparent pore-size distribution curve secured for a similar fragment in the "as-received"

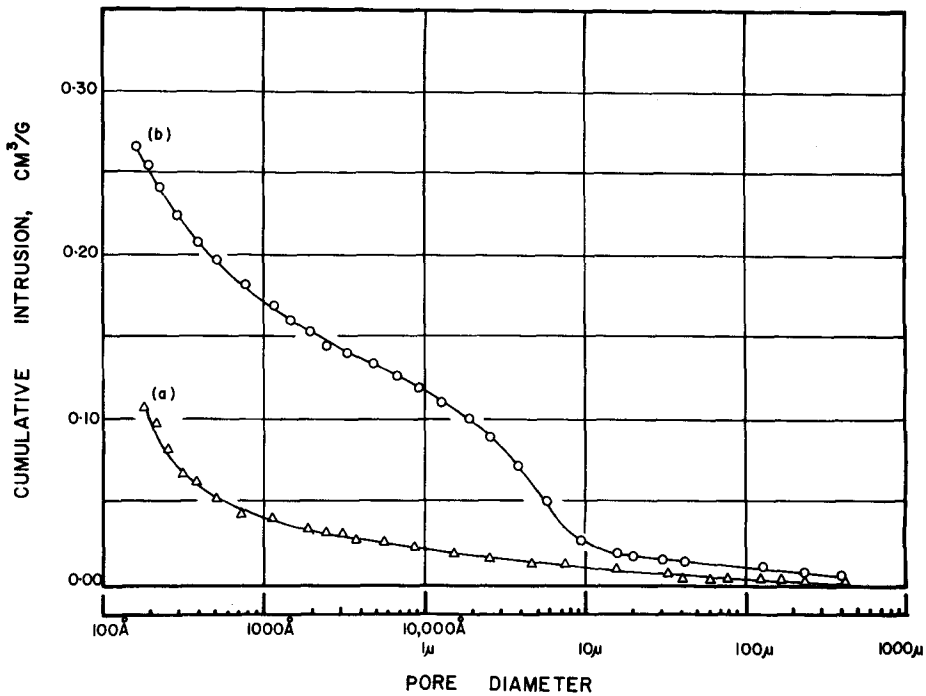


Fig. 5. Pore-size distribution curves for Bedford halloysite: (a) as received (moisture content 13% by weight); (b) after oven drying.

condition, i.e. at a moisture content of 13 per cent. The latter curve shows no indication of the bulge in the pore-size distribution reflecting the enhanced content of pores in the $10\ \mu$ to about $1\ \mu$ diameter range apparent from the curve for the oven-dry state as depicted in Fig. 5(b). The added content of pores in this diameter range, about $0.09\ \text{cm}^3/\text{g}$, is roughly the same as the increase in total porosity obtained on oven drying. It is tempting to speculate that the observed increase in porosity may be due to the partial unrolling of the several-micron long halloysite tubes as a consequence of oven drying.

Selected Indiana soils

It is well known that the influence of soil-forming processes often results in microstructural arrangements of clay and other soil particles such that relatively large proportions of void space are present in quite large pores. Comparatively few attempts have been made to document the distribution of pore sizes in soils, except in the special case of saturated soils whose "effective" pore size distributions are assessed by measuring the water removed from them under progressive increments of suction or pressure applied to the saturated system (see for example Vomocil, 1965).

In the present work an attempt was made to

characterize the pore-size distributions of the subsoils of several Indiana soils, which were sampled at field moisture contents somewhat less than saturation. The samples were oven dried and presumably representative fragments of about $\frac{1}{2}\ \text{g}$ in weight were selected for porosimetry. Of the soils employed, the Brookston, Miami, and Crosby soils are all residual soils derived from calcareous till; the Genessee soil is a terrace soil and the Fox is a "first-bottom" alluvial soil; all were sampled within a four square mile area within Tippecanoe Co., Indiana.

Table 2 indicates the very considerable total pore volume present after oven drying, of the order of $0.25\ \text{cm}^3/\text{g}$ for the soils tested. The reduction in porosity on oven drying (found to be of the order of $0.03\ \text{cm}^3/\text{g}$) is thus not of major significance. The pore-size distribution curves, shown in Fig. 6, are somewhat different from those of the reference clay samples previously considered. The porosity is in general, significantly greater in amount, and the pores are in general, significantly larger in diameter. Most of the pore space of all the soils is in pores of equivalent diameter greater than $1\ \mu$, and there is a significant content of pores greater than $100\ \mu$ for two of the soils, the Brookston and the Miami samples.

Another difference is that for the soils, essen-

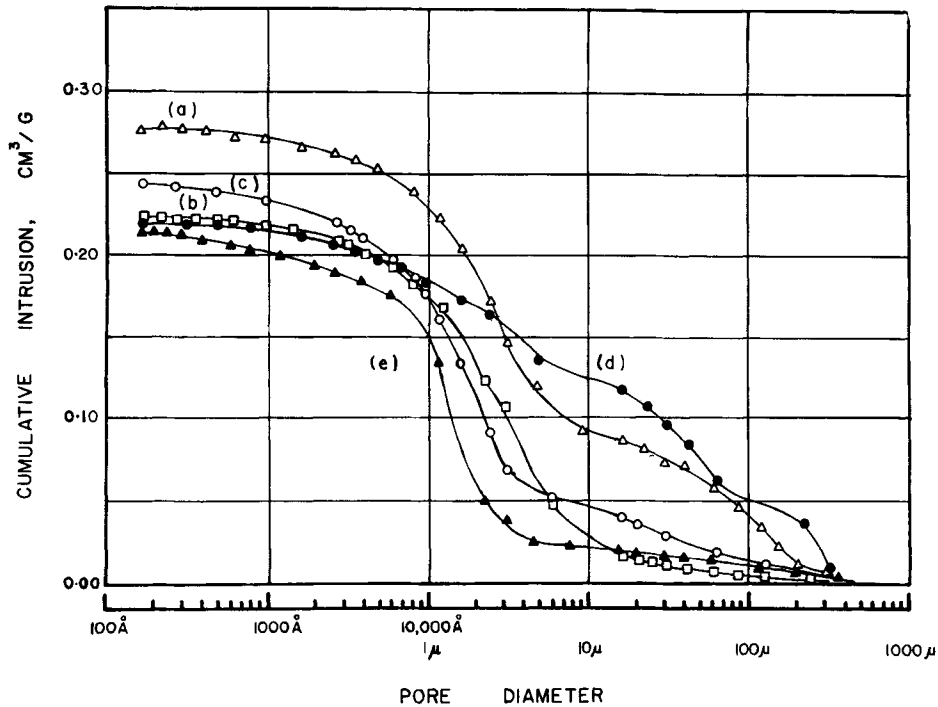


Fig. 6. Pore-size distribution curves for samples of selected Indiana subsoils: (a) Brookston silty clay loam; (b) Miami silt loam; (c) Crosby silt loam; (d) Genessee silt loam; (e) Fox silt loam.

tially all the pore space present in the oven-dried samples is available to mercury intruding at pressures below 15,000 psi. In fact the content of pores less than 1000 Å in equivalent diameter is negligible, despite the reasonably high clay content of these soils; only the Crosby and the Fox soils show as much as 0.01 cm³/g of pore space intruded in pores of equivalent diameter less than 1000 Å. This is in marked contrast to the reference clays, which contain principally pores having equivalent diameters less than about 3000 Å (except for the oven-dry halloysite, which appears to be a special case).

The data of Table 2 and the pore-size distribution curves of Fig. 6 represent results for individual approximately ½ g portions of the samples. Replicate runs on adjacent portions of the samples yield pore-size distribution curves very similar to each other in shape but which vary somewhat in overall porosity. It is apparent that any pore data secured for such small samples of material heterogeneous on a scale almost that of the sample size must yield indicative, rather than definitive, data. To secure more nearly representative data for soils of "coarse" structure, it would seem desirable to design a porosimeter capable of handling consider-

Table 2. Porosity characteristics of samples of selected Indiana subsoils

Soil series	Moisture content at sampling (%)	Total porosity (cm ³ /g)*	Pore space intruded by mercury (cm ³ /g)
Brookston silty clay loam	27	0.27 ₅	0.27 ₅
Miami silt loam	20	0.24 ₅	0.22 ₅
Crosby silt loam	21	0.25 ₅	0.24 ₅
Genessee silt loam	17	0.23 ₀	0.22 ₀
Fox silt loam	20	0.23 ₅	0.21 ₅

*Calculated from bulk density of oven-dried sample as measured in porosimeter using assumed specific gravity of 2.65.

ably larger maximum intruded volumes than the 0.2 cm³ limit of the instrument employed.

Clays sedimented from dispersed and from salt-flocculated suspensions

Samples of two commercial clays, Edgar Plastic kaolin from Florida, and Grundite, an illite-bearing clay from Illinois were employed. Portions of each were thoroughly dispersed in a milkshake machine, using a trace of Calgon as a dispersing agent, so as to form an aqueous suspension of about two per cent concentration by weight. A portion of each suspension was allowed to sediment undisturbed for a number of days until the supernatant solution was essentially clear. The remaining portion of each suspension was flocculated by the addition of sodium chloride (added with stirring until definite flocs were observed). The salt-flocculated suspensions were allowed to settle overnight, after which the supernatant liquid was essentially clear. The supernatant liquid in each case was siphoned off; additional liquid removed by aspirator suction over a Büchner funnel, and each of the samples was allowed to air-dry, forming a cake of the order of one-quarter inch in thickness at the bottom of the container. Portions of the material were sampled with a razor blade so as to attempt to include representative proportions of both fine and coarse material, and the samples were oven dried and pore-size distributions determined. The porosity data is given in Table 3 and the pore-size distribution curves in Fig. 7. Replicate samples give virtually identical results for the "salt-flocculated" samples, but some variation was noted in both the total porosity and pore-size distribution curves of the "dispersed" materials, presumably due to sampling difficulty.

It is apparent from the table that for both clays settlement in the salt-flocculated condition led to

a dried material with only about 60 per cent of the porosity retained by samples allowed to settle in the dispersed state. For both clays, Fig. 7 indicates that the bulk of the pore space assayed is in pores of significantly smaller sizes for the salt-flocculated material than for the material settled from the dispersed condition.

It is apparent from Table 3 that for both kinds of kaolinite preparation essentially all of the pore space present after oven drying was intruded by mercury; in contrast, for the illite preparations, especially the "dispersed" sample, a significant fraction of the pore space was not intruded, i.e. was present in pores of equivalent diameter less than about 160 Å or else was available to the surface only through channels smaller than this limiting value.

Figure 7(a) indicates that a small but significant content of quite large pores (5 μ to several hundred μ) occurs in the "dispersed" kaolinite clay; but large pores are essentially absent from the "dispersed" illite and particularly from both "flocculated" samples. The explanation for this effect appears to lie in the polydispersity of the clay, combined with the peculiar nature of the coarse kaolinite particles. The coarse size fraction of the kaolin, which has been studied extensively by Ormsby and Shartsis (1960), consists of particles which are composed of "books" of kaolinite plates rather than individual plates. A brief examination of the dried kaolin preparations by scanning electron microscopy* was made. It was apparent, as seen in Fig. 8, that the bottom layer of the sample prepared from the dispersed state consisted of "books" several to many microns in size, separated

*The scanning electron micrographs were supplied through the courtesy of Engis Equipment Co., Chicago, Illinois.

Table 3. Porosity characteristics of oven-dried commercial clay specimens

Sample	Condition of sedimentation	Total porosity* (cm ³ /g)	Pore space intruded by mercury (cm ³ /g)
Edgar Plastic kaolin (kaolinite)	Dispersed	0.47 ₀	0.45 ₀
	Flocculated	0.28 ₃	0.20 ₄
Grundite (illite)	Dispersed	0.27 ₀	0.22 ₀
	Flocculated	0.18 ₆	0.13 ₅

*Calculated from bulk density of oven-dried sample as measured in porosimeter using assumed specific gravity of 2.65 for the Edgar Plastic kaolin and 2.82 for the Grundite.

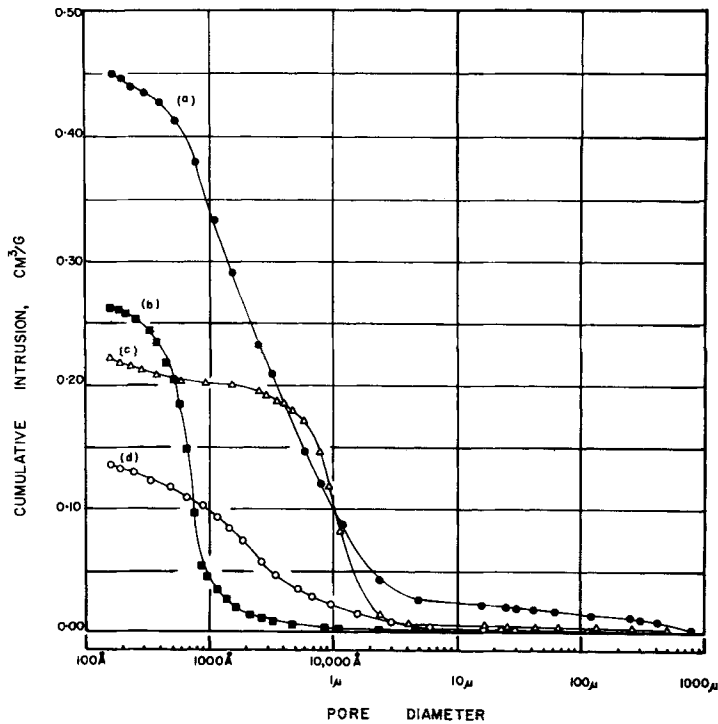


Fig. 7. Pore-size distribution curves for sedimented commercial clay samples: (a) Edgar Plastic kaolin, "dispersed"; (b) Edgar Plastic kaolin, "flocculated"; (c) Grundite, "dispersed"; (d) Grundite, "flocculated."

by pore spaces of the same order of magnitude. With the sample prepared from the flocculated state, the "books" are intimately surrounded by masses of finer particles, as seen in Fig. 9, and the resulting large spaces between "books" are not present. Figure 7 shows that besides the very large pores, the bulk of the pore space in the "dispersed" kaolinite ranges between limits of about 500 Å and 2 μ; in contrast, the bulk of the pore space in the "flocculated" preparation is confined to a significantly smaller and narrower range of perhaps 400 Å to about 1000 Å.

The general characteristics of the illite curves seem to be somewhat different from those of the corresponding kaolinite curves. The preparation made from the dispersed suspension seems to have the bulk of its observable porosity concentrated between about 500 Å and 2 μ in equivalent diameter, but the lesser pore space intruded in the "flocculated" sample is more or less uniformly spread over the whole of the available size range below 2 μ.

Compacted clays

A major feature of the utilization of clay and other soils for engineering purposes is the manner

in which they densify and become stronger with the application of mechanical compactive effort. In general, field compaction of soils involves the application of as many passes of heavy compaction equipment as required to attain a specific bulk density, after previously adjusting the loosened soil to an appropriate moisture content. For a given level of compactive effort the optimal moisture content for a given soil is determined by a standardized laboratory testing process involving compaction by the repeated impact of a weight allowed to fall on the soil from a specified height. Attempts to compact at moisture contents significantly different from the optimum result in less dense soils which are usually inferior in their ability to support loads.

The pore structure of compacted soils is of interest in defining the details of the compaction process and the state of compaction. In the present work, pore-size distributions have been determined for the Edgar Plastic kaolin commercial clay previously discussed, compacted by an impact compaction method essentially similar to standard procedures. Preparation of the samples involved thorough blending of the clay with a stated percentage of water in a twin-shell solid-liquid

blender, followed by compaction in three layers in a mold approximately 3.3 cm in diameter and 7.1 cm high. The compaction was effected by the dropping of a 1450-g cylindrical compaction hammer through a distance of 25.4 cm a specified number of times (usually 30) per layer. The method resembles, but does not exactly duplicate, those specified in ASTM D-698 and D-1557, Tests For Moisture-Density Relations of Soils.

The optimum moisture content of the kaolinite was found to be approximately 26 per cent for a standard compactive effort of 30 blows per layer. In general, the less the compactive effort, the higher the optimum moisture content for a given soil. Replicate samples of kaolinite were compacted using 30 blows per layer at moisture contents of 22, 26, and 30 per cent, i.e. significantly below the optimum, at the optimum, and significantly above the optimum for the level of effort employed. The results, as given in Table 4, show that the total porosity was virtually identical for all three moisture contents. Nevertheless, differences in behavior became obvious on oven drying the samples preliminary to mercury porosimetry. On drying, the sample compacted on the dry side of optimum moisture content did not shrink very much, but the other two samples suffered a considerable reduction in total pore space, and significantly, both wound up at the same porosity.

Examination of the pore-size distribution curves, Fig. 8(a), (b), and (c) in conjunction with the data of Table 4 suggests the following:

- (a) Despite the compactive effort and subsequent drying shrinkage, the pores of all samples remained large enough to be almost completely intruded by mercury at the 15,000 psi pressure available.
- (b) The samples compacted at or on the wet side of the optimum moisture content, Fig. 10(a)

and (b), displayed identical pore-size distribution characteristics after shrinkage on oven drying. The shape of the curve is identical with that shown in Fig. 7(b) for the same commercial clay sedimented from the flocculated condition, except that the content of pores of equivalent diameter between 300 and 600 Å is somewhat less.

- (c) Results for the sample compacted on the dry side of the optimum moisture content, Fig. 10(c), differed from those of the other two, by virtue of a significantly-increased content of pores between 2 μ and 1000 Å in diameter. Below 1000 Å, the curve was virtually identical to those of the other samples.

Additional samples of the same kaolinite were compacted at 26 per cent moisture content, but this time using lesser compactive effort; instead of 30 blows of the hammer per layer, 10 and 20 blows per layer were employed. Naturally, the specimens so compacted were less dense than the fully-compacted companion; Table 4 shows that, in fact, the pore space present after compaction was about 25 per cent and about 10 per cent greater, respectively. However, of importance is the differential shrinkage observed on oven drying; despite the fact that the more lightly compacted samples had "extra" pore space, they shrunk comparatively little on oven drying, while the "fully-compacted" sample, starting from a lower pore content, shrunk so as to lose 40 per cent of its lesser pore volume. The pore-size distribution curves for these samples, Fig. 10(d) and (e), are strikingly similar to the pore-size distribution curve for the heavily compacted kaolinite prepared on the dry side of optimum moisture (Fig. 10(c)) except that enhanced content of coarser pores extended to about 6 μ in equivalent diameter, rather than being limited to about 2 μ.

Table 4. Porosity characteristics of compacted kaolinite

Moisture content at compaction (%)	Compactive effort (blows per layer)	Total porosity in "as compacted" condition* (cm ³ /g)	Total porosity after oven drying† (cm ³ /g)	Porosity intruded by mercury (cm ³ /g)
26	30	0.31 ₈	0.22 ₈	0.21 ₂
30	30	0.33 ₁	0.22 ₉	0.21 ₃
22	30	0.32 ₅	0.29 ₈	0.26 ₂
26	10	0.39 ₄	0.34 ₁	0.31 ₂
26	20	0.34 ₈	0.32 ₃	0.29 ₆

*Bulk volume determined from volume of mold and dry weight of sample. Pore space calculated assuming specific gravity of 2.65.

†Calculated from bulk density of oven-dried sample as measured in dilatometer, assuming specific gravity of 2.65.

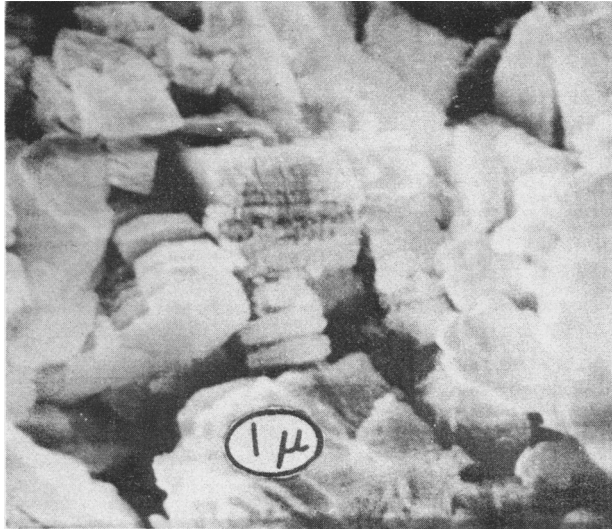


Fig. 8. Scanning electron micrograph of Edgar Plastic kaolin sedimented from the dispersed state: fracture surface of the lower portion of the cake, showing large pores between kaolinite "books."

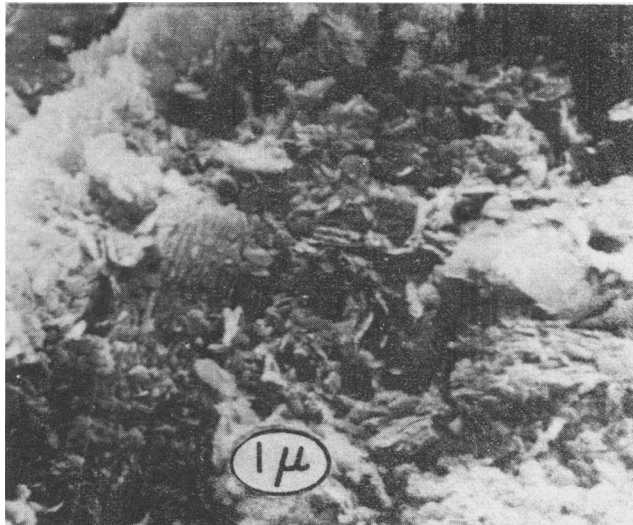


Fig. 9. Scanning electron micrograph of Edgar Plastic kaolin sedimented from the salt-flocculated state: fracture surface showing "books" surrounded by finer clay particles.

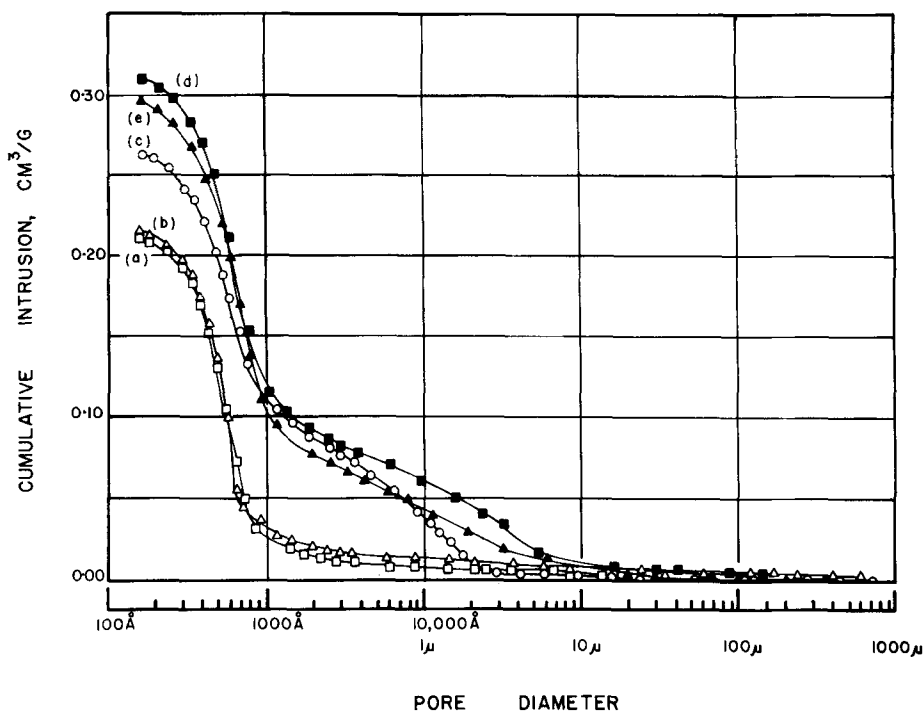


Fig. 10. Pore-size distribution curves for Edgar Plastic kaolinite compacted as follows: (a) 26% moisture content, 30 blows per layer; (b) 30% moisture content, 30 blows per layer; (c) 22% moisture content, 20 blows per layer; (d) 26% moisture content, 10 blows per layer; (e) 26% moisture content, 20 blows per layer.

It is hypothesized that there are two basic microstructures generated in compacting this kaolinite; if compaction is carried on at low moisture contents or with insufficient compactive effort for the moisture content present, a microstructure is produced which does not shrink appreciably on oven drying and in which there is retained a significant content of relatively-large diameter pores, ranging up to several microns. If the kaolinite is compacted either at optimum moisture or above optimum moisture, very significant shrinkage takes place on oven drying, and the resultant dried clay has pores only of equivalent diameters less than about 2000 Å. These results are consistent with the notion that the former samples have retained much of the structure of the individual, more-or-less spherical aggregates of particles formed in the mixing process, while the more effective compaction in the latter case has brought the clay particles into a more nearly homogeneous, quasi-parallel arrangement.

Alternate procedures for clay preparation

All of the pore-size distribution curves heretofore presented have been determined on samples

which have been dried by the conventional procedure of oven drying. For most well-structured natural soils of other than swelling characteristics, for geologically consolidated clays and shales, and for soils compacted on the dry side of the optimum moisture content, the reduction in porosity experienced on oven drying is not so severe as to seriously impede the interpretation of the pore-size distribution data. On the other hand, there are obviously problems when one has to deal with saturated or nearly saturated clays of high porosity and characteristically weak fabric, for which cases shrinkage may cause the information on pore-size distribution determined after oven drying to be completely misleading. For example, in soil mechanics, the question of the "in-situ" microstructure of saturated sensitive clays, and of the effects of remolding at high moisture content cannot be addressed profitably from a study of the pore size distribution in the oven-dry state, because of the very extensive shrinkage and consequent changes in the pore-size distribution function.

Of the several possible methods for removal of water from a clay mass without subjecting the mass

to shrinkage, two are being explored in research at Purdue University. The simpler procedure is "freeze-drying"; i.e. rapid freezing of the samples in liquid nitrogen or some other cryogenic medium followed by evacuation of the water under vacuum at a temperature sufficiently low that no unfrozen water can exist in the system. Thus, the influence of contraction of water menisci in pulling the clay particles into closer approach to each other as the sample dries is avoided. The major difficulty with this procedure is that of ensuring that no significant changes in the microstructure accompany the freezing process. For example, Ahlrichs and White (1967) have shown that rapid redistribution of interlayer water takes place on quick-freezing montmorillonite; whether this redistribution can affect the measured pore-size distribution is not yet known.

A second possible procedure involves arranging a dynamic program of temperature and pressure changes so that the water in the sample is slowly brought into the thermodynamic "critical region" without being expelled from the clay. In this region (temperature above 274°C and pressure greater than 216.4 bars) the meniscus marking the interface between liquid water in the pores of the sample and water vapor has disappeared, all water existing

as a single homogenous fluid phase. It is then possible to "distill" the water from the sample to a slightly colder region without the clay undergoing shrinkage. Once this process is complete, the sample can be slowly cooled and depressured without serious consequence.

A device for accomplishing this has been constructed at Purdue University by J. R. Hooper, and plans are underway for the construction of a second, modified system. Hooper has succeeded in preparing specimens of saturated clays of high porosity which have had their water removed in the critical region without change in total porosity, and without the presence of cracking or other mechanical disturbance. Figure 11 shows a pore-size distribution curve determined for one such specimen, a commercial Georgia kaolinite flocculated and settled in water acidified to pH 4.0. The total pore space was $0.50\text{ cm}^3/\text{g}$, all of which was intruded by mercury. It appears that about twenty per cent of the extensive pore space present is in pores greater than a micron in equivalent diameter, and comparatively little in pores with equivalent diameter less than 1000 \AA .

A saturated sample of Leda clay, a "quick" clay of considerable importance because of its widespread occurrence in Eastern Canada (Crawford,

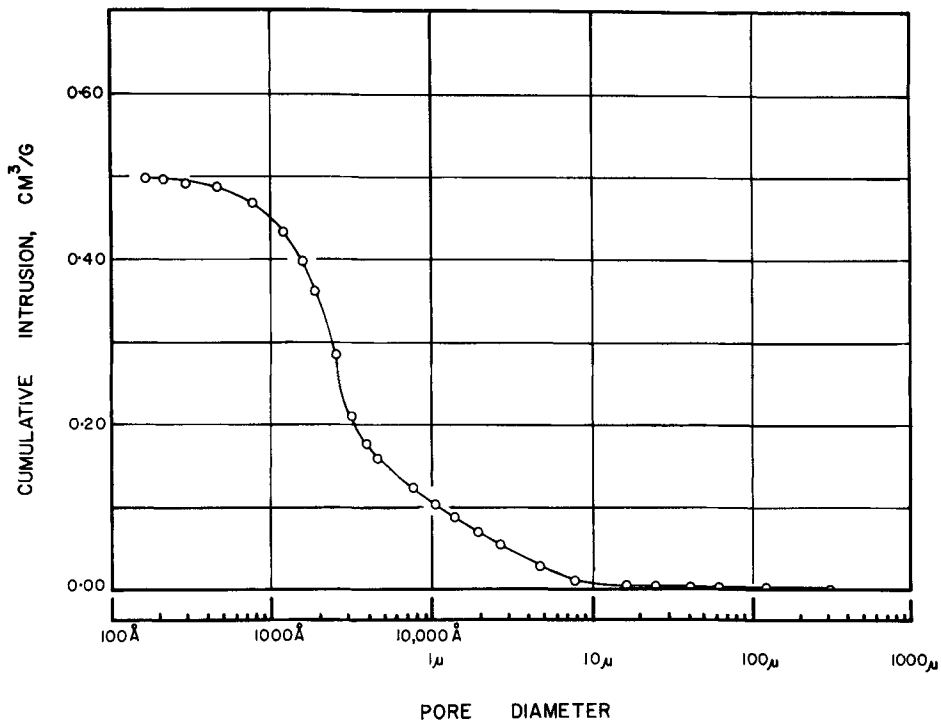


Fig. 11. Pore-size distribution curves for critical-region dried Georgia kaolin sample.

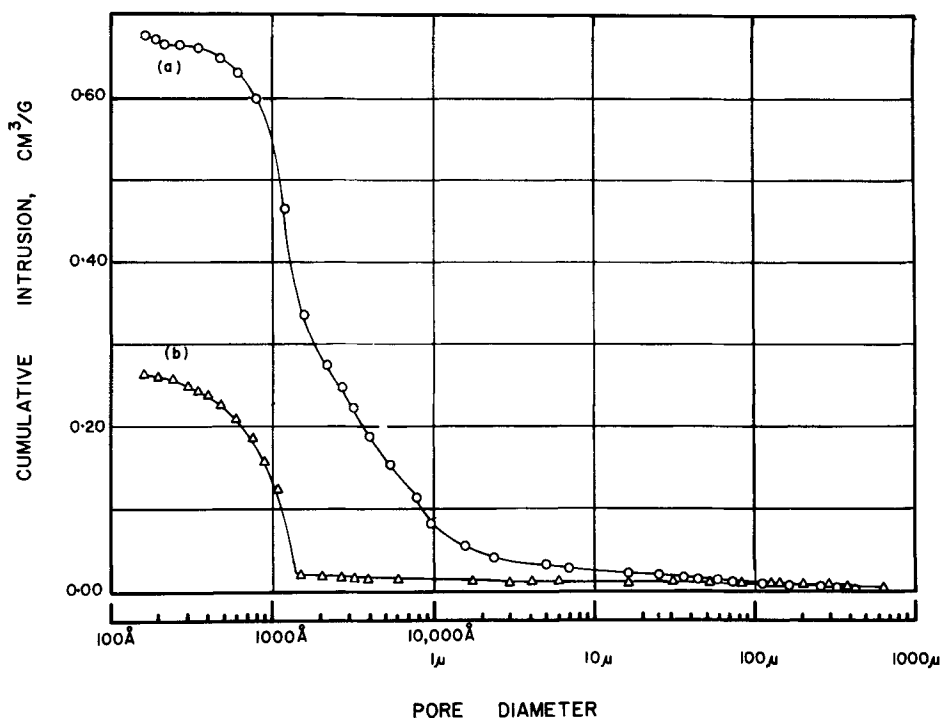


Fig. 12. Pore-size distribution curves for Leda clay; (a) critical-region dried; (b) oven-dried.

1968), was successfully dried through the critical region by Mr. D. W. Devenny, and the resulting pore-size distribution is given in Fig. 12(a). For comparison, another portion of the same material was oven dried. All of the 0.67 cm³/g pore space originally measured (natural moisture content was 68 per cent) was retained after critical-region drying, and was intruded by mercury; in contrast, a replicate portion dried in an oven shrunk to a porosity of only 0.28 cm³/g. Its pore-size distribution curve is shown in Fig. 12(b). Comparison of the two curves suggests that the shrinkage resulting from oven drying removed primarily the larger pores, i.e. pores of equivalent diameter greater than about 1500 Å. The distribution of pores of equivalent diameter less than this is about the same for both samples.

Mr. Devenny has recently succeeded in satisfactorily freeze-drying another sample of Leda clay without change in total pore space and has determined its pore-size distribution. The distribution curve he obtained is similar to that of the critical-region dried sample, Fig. 12(a), but differs from it slightly in that the concentration of pore volume marked by the nearly vertical slope of the curve in the region of 1000 Å or so is not present, and a slightly greater content of larger pores

between 1 and 3 μ is shown. The samples are not from the same batch of material and it is uncertain whether the differences reflect inherent differences in the samples prior to processing or artifacts of one or the other treatments. As yet there is no certain evidence that the pore-size distribution of either critical-dried material or freeze-dried material is identical to that preexisting in the saturated condition, although either is certainly a much better approximation to it than can be obtained after conventional drying treatment for samples of this nature.

CONCLUSION

It seems apparent that mercury porosimetry can provide a useful and potentially valuable measurement of the state of porosity in a given clay structure. Proper care is urged in experimental determination, and due caution should be exercised in interpreting the results in the light of uncertainties consequent on the pore shape model and on the required removal of water prior to the determination.

Note added in proof. A discussion of methods of removal of water without alteration of the fabric of clay has recently been given by J. E. Gillott (Gillott, J. E. (1969) Study of

the fabric of fine-grained sediments with the scanning electron microscope: *J. Sediment. Petrol.* **39**, 90–105).

Acknowledgment—I acknowledge with thanks the very competent technical assistance of Mrs. Patricia Mewhinney and Mr. D. N. Winslow.

REFERENCES

- Adamson, Arthur W. (1967) *Physical Chemistry of Surfaces* (2nd edn) Interscience, New York 747 pp.
- Ahlich, J. L., and White, J. L. (1962) Freezing and lyophilizing alters the structure of bentonite gels: *Science* **136**, 116–118.
- Crawford, Carl B. (1968) Quick clays of eastern Canada: *Eng. Geol.* **2**, 239–265.
- Kemball, C. (1946) On the surface tension of mercury: *Trans. Faraday Soc.* **42**, 526–537.
- Nicholas, M. E., Joyner, P. A., Tessem, B. M., and Olsen, M. D. (1961) The effects of various gases and vapors on the surface tension of mercury: *J. Phys. Chem.* **65**, 1373–1375.
- Ormsby, C. W. and Shartsis, J. M. (1960) Surface area and exchange capacity relation in a Florida kaolinite: *J. Am. Ceram. Soc.* **43**, 44–47.
- Padday, J. J. (1957) A new method for measuring the spreading coefficient of a liquid on a solid surface: *Proc. 2nd Intern. Congr. Surface Activity*, London **3**, 136–142.
- Ritter, H. L., and Drake, D. L. (1945) Pore-size distribution in porous materials: *Ind. Eng. Chem., Analyt. Ed.* **17**, 782–791.
- Vomocil, James A. (1965) Porosity: In *Methods of Soil Analysis* (Edited by C. A. Black) American Society of Agronomy, Madison, Wisconsin, Part 1, 299–314.
- Washburn, E. W. (1921) Note on a method of determining the distribution of pore sizes in a porous material: *Proc. Nat. Acad. Sci. U.S.* **7**, 115–116.
- Winslow, N. M. and Shapiro, J. J. (1959) An instrument for the measurement of pore-sized distribution by mercury penetration: *A.S.T.M. Bull.* **236**, 39–54.
- Yong, Raymond N. and Warkentin, Benno P. (1966) *Introduction to Soil Behavior*: Macmillan, New York, 439 pp.

Résumé—La connaissance de la distribution des dimensions des pores dans l'argile et les constituants du sol, est un élément utile dans la caractérisation microstructurale de tels matériaux. Les distributions de la dimension des pores et la porosité totale d'un certain nombre d'argiles de référence, se produisant naturellement dans les sous-sols, et les échantillons d'argile commerciaux préparés de différentes manières, ont été déterminés par la porosimétrie du mercure. L'étendue du diamètre équivalent du pore exploré, couvrait presque cinq ordres de grandeur, variant de plusieurs centaines de microns pour atteindre approximativement 150 Å. La méthode et ses hypothèses sont évaluées d'une façon critique, et les mesures de l'angle de contact de mercure sur les argiles fournissent des valeurs de 139° pour le montmorillonite et 147° pour la kaolinite et les argiles illite. Le degré de retrait par séchage au four préalablement à l'injection de mercure est évalué dans chaque cas et on s'aperçoit qu'il varie d'une valeur insignifiante pour atteindre un taux de 30 pour cent de l'espace du pore, cela dépend de l'état microstructural et du degré de saturation initial. Le développement des techniques pour l'élimination d'eau qui n'implique pas de modifications dans la structure du pore est exploré. Certains résultats préliminaires pour les argiles saturés, structurellement faibles, suggèrent que le séchage de la région critique et peut-être les méthodes de séchage par congélation, peuvent être pratiqués.

Kurzreferat—Eine Kenntnis der Verteilung der Porengrößen in Tonen und Erdböden ist ein wichtiges Element in der mikrostrukturellen Charakterisierung solcher Materiale. Die Porengrößenverteilungen und die Gesamtporosität einer Anzahl von Kontrolltonen, natürlich vorkommender Untergründe und auf verschiedene Weise bereiteter, handelsmässiger Tonproben wurden mittels Quecksilber-Porosimetrie bestimmt. Der Bereich untersuchter Porendurchmesser umfasste beinahe fünf Grössenordnungen, angefangen von einigen Hundert Mikrons bis hinunter zu etwa 150 Å. Dieses Verfahren und seine Voraussetzungen werden kritisch beurteilt, und Messungen des Kontaktwinkels des Quecksilbers an Tonen ergaben Werte von 139° für Montmorillonit und 147° für Kaolinit und Illit Tone. Das Ausmass der Schrumpfung durch Ofentrocknung vor dem Eindringen des Quecksilbers wurde jeweils eingeschätzt, und es wurde festgestellt, dass die Variation, je nach dem mikrostrukturellen Zustand und dem Masse an anfänglicher Sättigung, sich von unbedeutenden Werten bis hinauf zu 30 Prozent des Porenraumes bewegten. Die Entwicklung von Methoden für die Entfernung von Wasser ohne Veränderung der Porenstruktur wird erörtert. Vorläufige Resultate mit strukturell schwachen, gesättigten Tonen deuten darauf hin, dass Trocknung im kritischen Bereich und vielleicht Friertrocknungsverfahren von praktischer Bedeutung sein könnten.

Резюме—Распределение размеров пор в глине и почвах является для этих материалов важным элементом их микроструктурной характеристики. Распределение размеров пор и общая пористость для стандартных глин и подпочвенных образцов, а также для различно приготовленных образцов коммерческих глин были определены с помощью ртутного метода. Интервал найденных размеров эквивалентного диаметра пор покрывает почти пять порядков величины, от нескольких сотен микрон до примерно 150 Å. Сам метод и использованные в нем допущения критически оценены, а измерения контактного угла ртути на глинах дали

значения 139° для монтмориллонитовых и 147° для каолинитовых и гидрослюдистых глин. В каждом случае оценена степень сжатия при высушивании в печах до внедрения ртути и найдено, что в зависимости от микроструктурного состояния и степени первоначального насыщения она изменяется от незначительной до 30% объема пор. Рассмотрены возможности развития методов удаления воды без изменения пористой структуры. Некоторые предварительные данные для структурно слабо насыщенных глин указывают на практическую значимость высушивания в критической области, а также, возможно, и высушивания при замораживании.