Method-Dependent Values of Bulk, Grain, and Pore Volume as Related to Observed Porosity

GEOLOGICAL SURVEY BULLETIN 1203-D

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By G. EDWARD MANGER

EXPERIMENTAL AND THEORETICAL GEOPHYSICS

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Includes formulated differences for total and apparent porosity

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1966

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 15 cents (paper cover)

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By G. EDWARD MANGER

ABSTRACT

Observed values of porosity are derived from method-dependent values of bulk, grain, and pore volume. Formulated porosity differences show the relation of observed porosity to these method-dependent values. At very low porosity, differences in measured bulk volume, caused by method of measurement, result in differences in porosity values that are about equal to the excess of the greater over the lesser bulk volume, per unit bulk volume; thus at very low porosity, such porosity differences may be greater than the porosity. At very low porosity, apparent porosity, based on measured mercury-displacement bulk volume, can be forced to approximately equal apparent porosity, based on a greater measured water-displacement bulk volume, by not decreasing the volume of absorbed water (as a measure of pore volume) used for the mercury-displacement bulk volume according to the excess of the water-displacement over the mercury-displacement bulk volume. Omission of such a decrease, however, ignores the fact that pore volume is not determinable independently of bulk volume, and at higher porosity the omission results in greater excess of observed apparent over observed total porosity. With an increase in porosity there is a decrease in magnitude, as percent porosity, of the effect of method-dependent values of bulk volume. Experimental results show that an observed excess of total over apparent porosity for specimens of lapilli tuff from the Nevada Test Site is due largely to the fact that the density of the grain powder that is used for the total-porosity determination is not typical of the whole specimen. Of an observed excess of 0.96 percent total porosity, occluded pores constitute no more than 0.12 percent porosity and may be absent. Experimental results suggest that an excess of water-displacement over mercury-displacement bulk volume for some rocks may persist to low values of porosity.

INTRODUCTION

Observed total porosity and observed apparent (or effective) porosity of a porous medium depend upon the method used to measure bulk volume. An excess of total over apparent porosity is caused by occluded, or sealed-off, pores and by adsorption that may be occurring while grain-powder density is being determined to obtain total porosity. Additionally, certain experimental conditions, such as incomplete saturation of permeable pores during the test for apparent pore volume, may cause differences between observed total and apparent porosity.

Difference in values of total and apparent porosity, as a result of occluded pores, has been discussed in several reports, including those of Hartmann, Westmont, and Morgan (1926) and Fancher, Lewis, and Barnes (1933). Differences in observed porosity that result from method-dependent values of bulk volume have been considered in several reports, including those by Steinhoff and Mell (1924) and Hartmann (1926). Apparently, however, no study has been made of the relation of the combined effect of method-dependent determination of bulk, grain, and pore volumes to observed porosity. By means of a formulation of porosity differences, the present study considers the relation of observed porosity to a combination of such effects, including those of certain deficiencies of experimental procedure.

ACKNOWLEDGMENTS

The writer is indebted to Irwin Roman and Joel H. Swartz, geophysicists retired from the U.S. Geological Survey, who generously gave valuable suggestions and provided assistance in deriving the formulations in this report. Charles C. Hawley, of the Geological Survey, assisted in the experiments. The work on which this report is based was done by the Geological Survey on behalf of the Albuquerque Operations Office of the U.S. Atomic Energy Commission.

GENERAL RELATIONS OF BULK, PORE, AND GRAIN VOLUME TO POROSITY

ELEMENTS OF POROSITY DETERMINATION

Total porosity of a porous medium is a measure of its total void volume and is the excess of bulk volume over grain volume, per unit of bulk volume. Experimentally, total porosity is usually determined as the excess of grain density over bulk density, per unit of grain density. Apparent porosity, often called effective or net porosity, is a measure of the apparent void volume of a porous medium and is determined as the excess of bulk volume over grain volume and occluded-pore volume, per unit of bulk volume. The excess of bulk volume over grain volume and occluded-pore volume is determined by the fluid capacity of the permeable pores of the porous medium.

EFFECT OF BULK VOLUME ON POROSITY

Because pore volume is the excess of bulk volume over grain volume, values of pore volume vary with method-dependent values of bulk volume. If pore volume is considered to be constant, as is sometimes assumed, the effect of variation in values of bulk volume on values of total and apparent porosity may be stated as follows: At constant grain volume (constant grain density), an increase in bulk volume (decrease in bulk density) results in an increase in total porosity; at constant pore volume (as, for example, volume of absorbed water), an increase in bulk volume results in a decrease in apparent porosity. At constant grain volume (constant grain density), a decrease in bulk volume (increase in bulk density) results in a decrease in total porosity; at constant pore volume (as, for example, volume of absorbed water), a decrease in bulk volume results in an increase in apparent porosity.

RELATION OF SURFACE PORES TO METHOD OF BULK-VOLUME MEASUREMENT

Variations in bulk volume depend in part upon the degree to which surface pores are included in or excluded from the particular bulk-volume measurement. Surface pores, for lack of a better term, may be defined as those parts of pores which remain at the surface of a specimen after the grains have been sliced or abraded to shape the surface of the test specimen. The problem presented by surface pores is that, with a change in method of bulk-volume determination, the same incremental volume of surface pores is added to or subtracted from both pore volume and bulk volume, resulting in a change in the ratio of pore volume to bulk volume, or correspondingly, in a change in porosity.

METHODS OF BULK-VOLUME MEASUREMENT

DIMENSIONING

One can reason that the linear dimensioning of a geometrically shaped specimen should give the best value of bulk volume, provided that two conditions are met: (*a*) the specimen has a shape for which volume can be uniquely determined; (*b*) the shape is established by slicing cleanly through the rock without forming depressed surfaces. Such surfaces may be caused by plucking of grains or larger pieces of material from the specimen. Because in practice it is difficult to satisfy these conditions, the method of dimensioning is not generally used.

Dimensioned measurements of a specimen that is not exactly shaped can be expected to be too large, and hence the determined bulk volume would be too large. Likewise, dimensioning of a specimen from which surface grains have been plucked can be expected to show a bulk volume that is too large, because the surface reentrants that result from the plucking are included as bulk volume.

WATER DISPLACEMENT

In the water-displacement method a water-saturated specimen is freed of excess water by touching its surface with thoroughly moist absorptive paper; the specimen is then weighed in air. This weighing is immediately followed by immersing the specimen in water and weighing it while submerged. The difference in weight of the saturated specimen in air and in water is the weight of the water displaced, from which the volume of the displaced water, and hence the specimen, is obtainable. Frequently saturation and displacement are obtained by using, instead of water, liquids with low surface tension that provide better wettability.

The water-displacement bulk volume may be too large or too small. Consider that a nonporous specimen is exactly shaped geometrically and the resulting surface is smooth but wettable. Presumably the true bulk volume would be obtainable by dimensioning. Consider now that the usual procedure is followed and an attempt is made to saturate the specimen before it is immersed in water to obtain its bulk volume. Because the surface of the specimen is considered to be wettable, the residual water film that adheres to the saturated specimen before immersion may be expected to result in a bulk volume value that is too large.

This result might also be obtained for a very finely porous specimen or for a specimen whose surface appears macroscopically to be nonporous. On porous specimens, however, the surface water film tends to fill the hollows between the grains but to leave the apices of the grains free of water. As a result, the dimensioned volume of a geometrically shaped porous specimen usually exceeds the water-displacement bulk volume. Consequently, it may be expected that total porosity based on water-displacement bulk volume is usually less than total porosity based on a larger dimensioned bulk volume. For a constant pore volume, apparent (or effective) porosity based on water-displacement bulk volume usually exceeds apparent porosity based on dimensioned bulk volume.

MERCURY DISPLACEMENT

In the mercury-displacement determination of bulk volume, a specimen (generally of lower specific gravity than mercury) is forcibly submerged in a bottle full of mercury and the overflow mercury is considered to equal the bulk volume of the specimen. Because of its high specific gravity and fugacity, mercury tends to fill the surface pores of a specimen (Hartmann, 1926). Consequently, the volume of overflow mercury may indicate a minimum volume. The dimensioned bulk volume of a porous specimen usually exceeds the mercury-displacement bulk volume.

Not all investigators have reported that the mercury-displacement bulk volume is the smallest. For some specimens of refractory materials Steinhoff and Mell (1924) reported that they obtained a slightly greater mercury-displacement bulk volume than water-displacement bulk volume. Also, T. H. McCulloh (written commun., July 22, 1964) concluded that "the entrapment of air bubbles against the surface of a test specimen immersed in mercury leads invariably to a bulk volume determination that is erroneously large. The rougher the specimen surface, the higher the error." Accordingly, the mercury-displacement method of bulk-volume determination should be used only if such entrapment of air bubbles can be overcome.

A possible cause for a greater mercury-displacement than water-displacement bulk volume may be related to the removal of the excess water from the surface of the test specimen before it is immersed in water. If, in the process of removal of the excess water, some interior water, together with all the water of the surface pores, is removed, the water-displacement bulk volume may be less than the mercury-displacement bulk volume.

Although bulk volume based on mercury displacement may represent the smallest bulk volume, it does not necessarily follow that it is too small. As was mentioned, if the surfaces of the porous specimen are macroscopically smooth, the water-displacement bulk volume may be too large, because of a water film which adheres to the saturated specimen before it is immersed. For such a specimen, the mercury-displacement bulk volume may be the best value.

PORE VOLUME AND GRAIN VOLUME

Neither the total nor the apparent pore volume of a rock specimen is determinable independently of the bulk volume. The total pore volume is the excess of the method-dependent bulk volume over grain volume. Similarly, although it may not be immediately obvious, apparent pore volume is the excess of the method-dependent bulk volume over grain volume and occluded-pore volume. Consider, for example, that the bulk volume of a specimen is obtained by dimensioning, but the apparent pore volume is measured by the exhaustion of pore air into the mercury vacuum of a Washburn-Bunting porosimeter. The value for the volume of pore air nevertheless is the excess of the value for the mercury-submerged bulk volume over the grain volume and occluded-pore volume.

Although the fraction of surface pores included in or excluded from pore volume depends upon the method of measuring bulk volume, method-dependent values of bulk volume involve more than the volume of surface pores. Observed total and apparent pore volumes may therefore differ from the most acceptable pore volumes by more than the volume of surface pores.

Grain volume can be precisely determined if adsorption of water by the grain powder during the pycnometric determination of its

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volume is negligible and if the powder includes the whole specimen or is typical of the specimen. Nutting (1930) stated that adsorption of water by very finely powdered quartz grains during the pycnometric determination of the powder volume may cause an error of 1 or 2 percent in the grain density, although data to substantiate this point were not presented.

FORMULATED POROSITY DIFFERENCES

BASIC VARIABLES OF POROSITY DIFFERENCES

To formulate differences among observed porosities, it is necessary for the experimentally determined bulk and grain densities of the total porosities and the experimentally determined pore and bulk volumes of the apparent (or effective) porosities to be referred to the same variables. This is done by expressing the experimental porosities in terms of two variables—bulk volume and grain volume.

QUANTITIES OF FORMULATED POROSITY DIFFERENCES

In the development of the formulated porosity differences, bulk and grain volumes are related to ideal quantities and to quantities based on measurements of specimens. These quantities are given in the following list.

Symbol	Quantity	Method of determination
	Ideal quantities and quantities independent of a specimen	
V_b	Volume of specimen	
D_b	Density of specimen	
V_g	Volume of grains of specimen	
D_g	Density of grains of specimen	
V_p	Volume of powder portion of specimen	
D_p	Density of powder portion of specimen	
D_w	Density of water (obtained from tables relating density to temperature).	
D_m	Density of mercury (obtained from tables relating density to temperature).	
W_c	Weight of pycnometer, dry	
W_{cw}	Weight of pycnometer filled with water	
	Quantities based on measurements on a bulk specimen	
W'	Specimen weight, weight of dry specimen or bulk weight, or weight of grains, all equal in value.	Weighed in air.
W'_s	Weight of water-saturated specimen	Specimen evacuated, then saturated with water and weighed in air.
W'_{si}	Weight of saturated specimen in water	Weighed by suspended immersion.
V'_w	Bulk volume by water displacement	$(W'_s-W'_{si})/D_w$.
W'_m	Weight of mercury displaced by specimen	Capture and weighing.
V'_m	Bulk volume by mercury displacement	W'_m/D_m.
V'_v	Total void volume, defined as excess of water-displacement bulk volume over ideal grain volume, or $V'_v=V'_w-V_g$.	
V'_{vw}	Apparent void (pore) volume by water absorption	$(W'_s-W')/D_w$.
V'_{vm}	Apparent void (pore) volume adjusted for mercury-displacement bulk volume.	$V'_{vw}-(V'_w-V'_m)$.
D'_w	Bulk density by water displacement	W'/V_w'.
D'_m	Bulk density by mercury displacement	W'/V'_m.

Symbol	Quantity	Method of determination
Quantities based on measurements on powdered portion of specimen		
W''_c	Weight of pycnometer containing powder	Weighed in air.
W''	Weight of powder	$W''_c - W_c$.
W''_{cw}	Weight of pycnometer containing powder and water	Weighed in air.
W''_w	Weight of water displaced by powder	$W_{cw} - W_c - (W''_{cw} - W''_c)$.
V''	Volume of powder	W''_w / D_w.
D''	Density of powder	W''/V''.

RELATION BETWEEN SPECIMEN GRAIN VOLUME AND DENSITY AND GRAIN-POWDER VOLUME AND DENSITY

If the powder is typical of the specimen, the weight of the grains in the specimen is greater than the weight of the powdered portion by a factor k, so that

$$W' = kW'', \text{ where } k \geqq 1 \tag{1}$$

As grain volume is proportional to weight,

$$V_g = kV_p \tag{2}$$

and

$$D_p = D_g = W'/V_g \tag{3}$$

If, during pycnometry, water is adsorbed by the grain powder, there is an apparent decrease in the measured volume of the powder. This decrease introduces the factor a, whereby

$$kV'' = k(1-a)V_p = (1-a)V_g, \text{ where } 0 \leqq a < 1 \tag{4}$$

and

$$D'' = W''/V'' = kW''/k(1-a)V_p = W'/(1-a)V_g = D_g/(1-a) \tag{5}$$

RELATION BETWEEN APPARENT AND TOTAL VOID (PORE) VOLUME

Occluded pores cause the apparent void, or pore, volume as determined by water absorption (V'_{vw}) to be less than the total void volume (V'_v), or less than $V'_w - V_g$. A smaller void volume corresponds to a larger grain volume by a factor b. Hence,

$$V'_{vw} = V'_w - (1+b)V_g, \text{ where } 0 \leqq b \tag{6}$$

RELATION BETWEEN WATER-DISPLACEMENT AND MERCURY-DISPLACEMENT BULK VOLUME

In a recent study (Manger, 1965), bulk volume by water displacement was found usually to exceed bulk volume by mercury displacement, although for one specimen the mercury-displacement bulk volume was in excess. The bulk-volume relation is therefore expressed as

$$\frac{V'_w - V'_m}{V'_m} = \gamma \tag{7}$$

or

$$V'_w / V'_m = 1 + \gamma \tag{8}$$

Usually γ is small, and may be negative, zero or positive.

If apparent pore volume is obtained as the excess of the water-displacement bulk volume over the volume of absorbed water, the value of apparent pore volume used for mercury-displacement bulk volume should be adjusted according to the excess or deficiency of water-displacement bulk volume with respect to mercury-displacement bulk volume. If this adjustment is made, then

$$V'_{vm} = V'_{vw} - (V'_w - V'_m) = V'_{vw} - \gamma V'_m \tag{9}$$

RELATION OF OBSERVED TO FORMULATED POROSITIES

Total porosity ϕ_{tw} based on water-displacement bulk volume usually is obtained by determination of grain and bulk density and is expressed as

$$\phi_{tw} = \frac{D'' - D'_w}{D''} \tag{10}$$

Observed total porosity so obtained is related to formulated porosity based on bulk and grain volumes by means of volume and density relations in the lists of quantities and equation 5. The relation is is expressed as

$$\phi_{tw} = \frac{D'' - D'_w}{D''} = \frac{\frac{W'}{D'_w} - \frac{W'}{D''}}{\frac{W'}{D'_w}} = \frac{V'_w - (1-a)V_g}{V'_w} \tag{11}$$

Total porosity ϕ_{tm} based on mercury-displacement bulk volume likewise usually is obtained by the determination of grain and bulk density and is expressed as

$$\phi_{tm} = \frac{D'' - D'_m}{D''} \tag{12}$$

Observed total porosity so obtained is related to formulated porosity based on bulk and grain volumes by means of volume and density relations in the lists of quantities and equation 5. The relation is expressed as

$$\phi_{tm}=\frac{D''-D'_m}{D''}=\frac{\frac{W'}{D'_m}-\frac{W'}{D''}}{\frac{W'}{D'_m}}=\frac{V'_m-(1-a)V_g}{V'_m} \tag{13}$$

Apparent porosity ϕ_{ew} based on water-displacement bulk volume is obtained by determination of apparent pore volume and bulk volume and is expressed as

$$\phi_{ew}=\frac{V'_{vw}}{V'_w} \tag{14}$$

Observed apparent porosity so obtained is related to formulated porosity based on bulk and grain volumes by means of volume relations in equation 6 and is expressed as

$$\phi_{ew}=\frac{V'_{vw}}{V'_w}=\frac{V'_w-(1+b)V_g}{V'_w} \tag{15}$$

Apparent porosity ϕ_{em} based on mercury-displacement bulk volume is obtained by determination of apparent pore volume and bulk volume and is expressed as

$$\phi_{em}=\frac{V'_{vm}}{V'_m} \tag{16}$$

Observed porosity so obtained is related to formulated porosity based on bulk and grain volume by means of volume relations of equations 9 and 6 and is expressed as

$$\begin{aligned}\phi_{em}&=\frac{V'_{vm}}{V'_m}=\frac{V'_{vw}-(V'_w-V'_m)}{V'_m}\\&=\frac{V'_w-(1+b)V_g-(V'_w-V'_m)}{V'_m}\\&=\frac{V'_m-(1+b)V_g}{V'_m}\end{aligned} \tag{17}$$

If the adjustment by means of equation 9 for the value of pore volume used for mercury-displacement bulk volume is not made, the relation of observed to formulated porosity in equation 17 becomes

$$\phi_{em_1}=\frac{V'_w-(1+b)V_g}{V'_m} \tag{18}$$

This is equivalent to the equation

$$\phi_{em_1}=\frac{V'_{vw}}{V'_m}, \tag{19}$$

as equation 6 designates that $V'_{vw}=V'_w-(1+b)\ V_g$.

EXTENSION OF CERTAIN DEFINITIONS

As previously mentioned (p. D7), adsorption of water by the grain powder during pycnometry results in an apparent decrease in grain volume. The definition of factor a, where $0\leqq a<1$, can be extended to include all experimental conditions that cause an apparent decrease in grain volume, or an apparent increase in grain density, and consequently an increase in the value of total porosity. Also, as was mentioned, the presence of occluded pores causes apparent pore volume to be less than total pore volume. The definition of the factor b where $0\leqq b$, can be extended to include all experimental conditions that cause an apparent decrease in pore volume, or an apparent increase in grain volume, and consequently a decrease in the value of apparent porosity. Thus both factors a and b signify an increase in the value of total porosity over that of apparent porosity.

Conditions that cause an excess in the value of total porosity over apparent porosity and their relation to the factors a and b are listed as follows:

Condition	*Indicative factor*
Adsorption of water by the grain powder	a
Grain-powder density greater than density of the whole specimen	a
Occluded pores present	b
Incomplete saturation of the permeable pores as a measure of pore volume	b

There is one known experimental condition other than measurement error that can result in a seeming excess of apparent over total porosity. This condition arises if the grain-powder density is less than the grain density of the specimen. In terms of equations 4 and 5, this is equivalent to an increase in the volume of grain powder, or $kV''=(1+a)\ V_g$ and $D''=D_g/(1+a)$. To include this experimental condition in the preceding equations would require changing the limits of the factor a to show $0\geqq a$. Because the development of porosity-difference equations is facilitated by restricting the value of factor a to $0\leqq a<1$, the difference equations in the following section do not include the condition for deficient grain-powder density.

DIFFERENCE EQUATIONS

Difference equations are based on two total porosities and two apparent (or effective) porosities (ϕ_{tw}, ϕ_{tm}, ϕ_{ew}, and ϕ_{em}), as is shown in table 1. These difference equations are derived from equations 11, 13, 15, and 17, where the basic quantities are bulk volume and grain volume. As was mentioned, the factor a of equation 4 takes into account the effect of adsorption of water during the pycnometric determination of grain-powder density and all other conditions that increase the value of total porosity. The factor b of equation 6 allows for the effect of occluded pores and all other conditions that decrease the value of apparent (or effective) porosity. The factor γ indicates the relation between values of bulk volume as determined by water displacement and mercury displacement.

SIGNIFICANCE OF FORMULATED POROSITY DIFFERENCES

CHANGES IN VALUES OF POROSITY DIFFERENCE WITH VARYING POROSITY

Grain volume, or V_g, in table 1 appears only in the numerator of the fractional terms that are equated with observed porosity differences, and V_g decreases as porosity increases. Thus it follows that as porosity increases, there is a decrease in the excess of observed porosity based on water-displacement bulk volume over observed porosity based on mercury-displacement bulk volume. As porosity decreases, there is an increase in the excess of observed porosity based on water-displacement bulk volume. In the virtual absence of porosity, where $V_g \approx V'_w$, for no adsorption and no occluded pores $(0=a=b)$, differences in porosity values, except for the $\phi_{tw}-\phi_{ew}$ and $\phi_{tm}-\phi_{em}$ zero differences, are equal to about γ, where, as indicated by equation 7, $\gamma=(V'_w-V'_m)/V'_m$.

EFFECT OF USING THE SAME (UNADJUSTED) PORE VOLUME FOR APPARENT POROSITY BASED ON MERCURY-DISPLACEMENT AND WATER-DISPLACEMENT BULK VOLUME

At low porosity the value of apparent porosity based on mercury-displacement bulk volume can be forced to approximately equal the value of apparent porosity based on water-displacement bulk volume by not applying the adjustment indicated in equation 9, that is, by not decreasing the volume of absorbed water (as a measure of pore volume) by the excess of water-displacement over mercury-displacement bulk volume. If this decrease is neglected, those porosity differences that contain the quantity ϕ_{em} are decreased by the amount γ. For example, in table 1, for no adsorption and no occluded pores, if the decrease or adjustment is included, $\phi_{tw}-\phi_{em}=\gamma V_g/V'_w$. If the decrease is omitted, $\phi_{tw}-\phi_{em}=(\gamma V_g/V'_w)-\gamma$. Because $V_g \approx V'_w$ at low porosities, $(\gamma V_g/V'_w)-\gamma \approx 0$ and seemingly $\phi_{tw}-\phi_{em} \approx 0$.

That such equality of porosity is forced is readily shown. According to table 1, the differences in values of total porosity solely because of the bulk-volume effect—that is, for no adsorption and no occluded

TABLE 1.—*Porosity difference equations*

Observed difference: ϕ_{tw}=total porosity and ϕ_{ew}=apparent porosity, based respectively on water-displacement bulk density and bulk volume; ϕ_{tm}=total porosity and ϕ_{em}=apparent porosity, based respectively on mercury-displacement bulk density and bulk volume.

Formulated (or equivalent) difference: a=adsorption factor—includes all conditions that increase the value of total porosity; b=occluded-pore factor—includes all conditions that decrease the value of apparent porosity; V_g=grain volume; V'_w=bulk volume by water displacement; V'_m=bulk volume by mercury displacement; $\gamma=(V'_w-V'_m)/V'_m$. For no adsorption and no occluded pores, 0=a=b.

Observed difference	Formulated (or equivalent) difference resulting from method-dependent values of bulk volume, adsorption, and occluded pores			
	Adsorption effective and occluded pores present	Adsorption effective but occluded pores absent	Adsorption not effective but occluded pores present	No adsorption and no occluded pores
$\phi_{tw}-\phi_{ew}$	$(a+b)V_g/V'_w$	$a\ V_g/V'_w$	$b\ V_g/V'_w$	0
$\phi_{tw}-\phi_{tm}$	[1]	$\gamma\ (1-a)\ V_g/V'_w$	[1]	$\gamma\ V_g/V'_w$
$\phi_{tw}-\phi_{em}$ [2]	$[\gamma(1+b)+(a+b)]\ V_g/V'_w$	$(\gamma+a)\ V_g/V'_w$	$[\gamma(1+b)+b]\ V_g/V'_w$	$\gamma\ V_g/V'_w$
$\phi_{ew}-\phi_{tm}$	$[\gamma(1-a)-(a+b)]\ V_g/V'_w$	$[\gamma(1-a)-a]\ V_g/V'_w$	$(\gamma-b)\ V_g/V'_w$	$\gamma\ V_g/V'_w$
$\phi_{ew}-\phi_{em}$ [2]	[1]	[1]	$\gamma(1+b)\ V_g/V'_w$	$\gamma\ V_g/V'_w$
$\phi_{tm}-\phi_{em}$ [2]	$(1+\gamma)(a+b)\ V_g/V'_w$	$(1+\gamma)\ a\ V_g/V'_w$	$(1+\gamma)\ b\ V_g/V'_w$	0

[1] Observed porosity difference not applicable.

[2] For apparent porosity based on mercury-displacement bulk volume, the volume of absorbed water, as a measure of pore volume, is decreased according to the excess of water-displacement over mercury-displacement bulk volume.

pores—is $\phi_{tw}-\phi_{tm}=\gamma V_g/V'_w$. Consequently at very low porosity, where $V_g \approx V'_w$, $\phi_{tw}-\phi_{tm} \approx \gamma$. For no adsorption and no occluded pores, however, total and apparent porosity based on mercury-displacement bulk volume must be equal, or $\phi_{tm}=\phi_{em}$. If ϕ_{tm} is substituted for ϕ_{em} in the equation $\phi_{tw}-\phi_{em} \approx 0$ in the previous paragraph where the adjustment is not made, it seems that $\phi_{tw}-\phi_{tm} \approx 0$. But as mentioned, table 1 shows that in the absence of adsorption and occluded pores, at very low porosity $\phi_{tw}-\phi_{tm} \approx \gamma$.

Where the mentioned adjustment or decrease by means of equation 9 is not made, apparent porosity based on mercury-displacement bulk volume, or ϕ_{em}, usually exceeds all other porosity values, provided that the water-displacement bulk volume is greater than the mercury-displacement bulk volume. This excess becomes greater as porosity increases. This is because omission of this decrease causes all differences that contain the quantity ϕ_{em} to be diminished by the amount γ. As an example, consider the $\phi_{tw}-\phi_{tm}$ difference of table 1 for no adsorption and no occluded pores. If adjustment for pore volume is not made, $\phi_{tw}-\phi_{tm}=(\gamma V_g/V'_w)-\gamma$. As porosity increases, V_g and the V_g/V'_w ratio decrease, and the $\phi_{tw}-\phi_{em}$ difference becomes more negative, or the excess of observed apparent porosity (ϕ_{em}) over observed total porosity (ϕ_{tw}) increases. Where adsorption is effective and occluded pores are present, it is possible that $\phi_{tw}-\phi_{em}>0$, that is,

$$\frac{\gamma(1+b)+(a+b)}{V'_w} V_g-\gamma>0.$$

This, however, requires large values for the factors a and b.

EQUALITY OF TOTAL AND APPARENT POROSITY

According to table 1, for no adsorption and no occluded pores, $\phi_{tw} - \phi_{ew} = \phi_{tm} - \phi_{em} = 0$. However, $\phi_{tw} - \phi_{tm} = \gamma V_g/V'_w$. Thus equality of total and apparent porosity signifies only that occluded pores are absent, but not that the best value of porosity has been obtained. Obtaining the best value of porosity depends upon obtaining the best value of bulk volume.

LARGER APPARENT-POROSITY DIFFERENCE THAN TOTAL-POROSITY DIFFERENCE

Table 1 shows that where adsorption is effective and the value of water-displacement bulk volume is greater then the value of mercury-displacement bulk volume, or $V'_w>V'_m$, the total-porosity difference $\phi_{tw} - \phi_{tm}$ is $\gamma(1\text{-}a)V_g/V'_w$. Where occluded pores are present and $V'_w>V'_m$, the apparent-porosity difference $\phi_{ew} - \phi_{em}$ is $\gamma(1+b)V_g/V'_w$. The excess of apparent-porosity difference over total-porosity difference is therefore $\gamma(a+b)V_g/V'_w$. As porosity increases, V_g decreases

TABLE 2.—*Total and apparent porosity of lapilli tuff, subunit T, Paintbrush Tuff, the Nevada Test Site, Nev.*

Specimen	Grain-powder density (g cm^{-3}) D''	Pore volume (ml) by water absorption V'_{sw}	Bulk volume (ml) by displacement of—		Bulk density dry (g cm^{-3}) based on bulk volume		γ[1]	Porosity (percent)			
								Total, based on bulk density		Apparent, based on bulk volume	
			Water V'_w	Mercury V'_m	Water D'_w	Mercury D'_m		Water ϕ_{tw}	Mercury ϕ_{tm}	Water ϕ_{sw}	Mercury[2] ϕ_{sm}
15	2.232	1.802	4.394	4.333	1.342	1.361	0.014	39.87	39.02	41.01	40.18
2	2.273	1.511	4.253	4.170	1.490	1.519	.020	34.45	33.17	35.53	34.24
7	2.279	1.570	4.895	4.826	1.554	1.576	.014	31.81	30.85	32.07	31.10
13	2.304	2.343	6.202	6.235	1.396	1.388	−.005	39.41	39.76	37.78	38.11
8	2.314	2.401	5.912	5.819	1.360	1.382	.016	41.23	40.28	40.61	39.66
1	2.319	1.994	5.103	5.025	1.425	1.447	.016	38.55	37.60	39.07	38.13
3	2.323	1.509	4.070	4.011	1.448	1.470	.015	37.67	36.72	37.08	36.15
4	2.361	2.685	6.554	6.436	1.356	1.381	.018	42.57	41.51	40.97	39.89
10	2.442	2.803	6.756	6.615	1.360	1.389	.021	44.31	43.12	41.49	40.24
11	2.502	1.449	4.629	4.493	1.585	1.633	.030	36.65	34.73	31.30	29.22
Average	2.335		5.277	5.196			.016	38.65	37.68	37.69	36.69
Average without specimens 10 and 11	2.301		5.173	5.107			.013	38.20	37.36	38.02	37.18

[1] $\gamma = \frac{V'_w - V'_m}{V'_m}$.

[2] For the apparent porosity based on mercury-displacement bulk volume, the pore volume indicated by the volume of absorbed water is decreased by the excess of water-displacement over mercury-displacement bulk volume, that is, $V'_{sm} = V'_{sw} - (V'_w - V'_m)$.

and the value of the excess $\gamma(a+b)V_g/V'_w$ decreases. The fact that the total-porosity difference is smaller than the apparent-porosity difference does not mean that total porosities are better approximations to the true value of porosity, because obtaining the best value of porosity depends upon obtaining the best value of bulk volume.

EXPERIMENTAL ILLUSTRATION OF THE FORMULATED POROSITY DIFFERENCES

EXCESS OF TOTAL OVER APPARENT POROSITY

Porosity data for lapilli tuff from the Nevada Test Site have previously been reported (Manger, 1965). These data are shown in table 2 with the addition of values of γ. Table 3 lists porosity differences derived from table 2 and includes values for $\phi_{tw}-\phi_{ew}$, or values for the excess of total over apparent porosity where both porosities are based on water-displacement bulk volume. An average excess of total porosity of 0.96 percent porosity according to table 1 suggests that adsorption is effective or that occluded pores are present. Deficiencies and excesses of total porosity in table 3, however, are apparently related to grain-powder density, or D''. Figure 1 indicates a strong dependence of deficiencies and excesses of total porosity on grain-powder density.

TABLE 3.—*Porosity differences of lapilli tuff, subunit T, Paintbrush Tuff, Nevada Test Site, Nev.*

Specimen	D''[1] (g cm^{-3})	$\phi_{tw}-\phi_{ew}$[2] (percent)	$\phi_{tw}-\phi_{tm}$[3] (percent)	$\phi_{ew}-\phi_{em}$[4] (percent)
15	2.232	−1.14	0.85	0.83
2	2.273	−1.08	1.28	1.29
7	2.279	−.26	.96	.97
13	2.304	1.63	−.35	−.33
9	2.314	.62	.95	.95
1	2.319	−.52	.95	.94
3	2.323	.59	.95	.93
4	2.361	1.60	1.06	1.08
10	2.442	2.82	1.19	1.25
11	2.502	5.35	1.92	2.08
Average	2.335	.96	.98	1.00
Average without specimens 10 and 11	2.301	.18	.83	.83

[1] Grain-powder density.
[2] Total porosity based on water-displacement bulk density minus apparent porosity based on water-displacement bulk volume.
[3] Total porosity based on water-displacement bulk density minus total porosity based on mercury-displacement bulk density.
[4] Apparent porosity based on water-displacement bulk volume minus apparent porosity based on mercury-displacement bulk volume.

As mentioned, there is only one known cause, other than measurement error, for a deficiency of total porosity with respect to apparent porosity, namely, that the density of the grain powder used for the grain-density determination is less than the grain density of the specimen. Because of this indicated causal relationship, the coefficient of determination r^2, where r is the coefficient of correlation

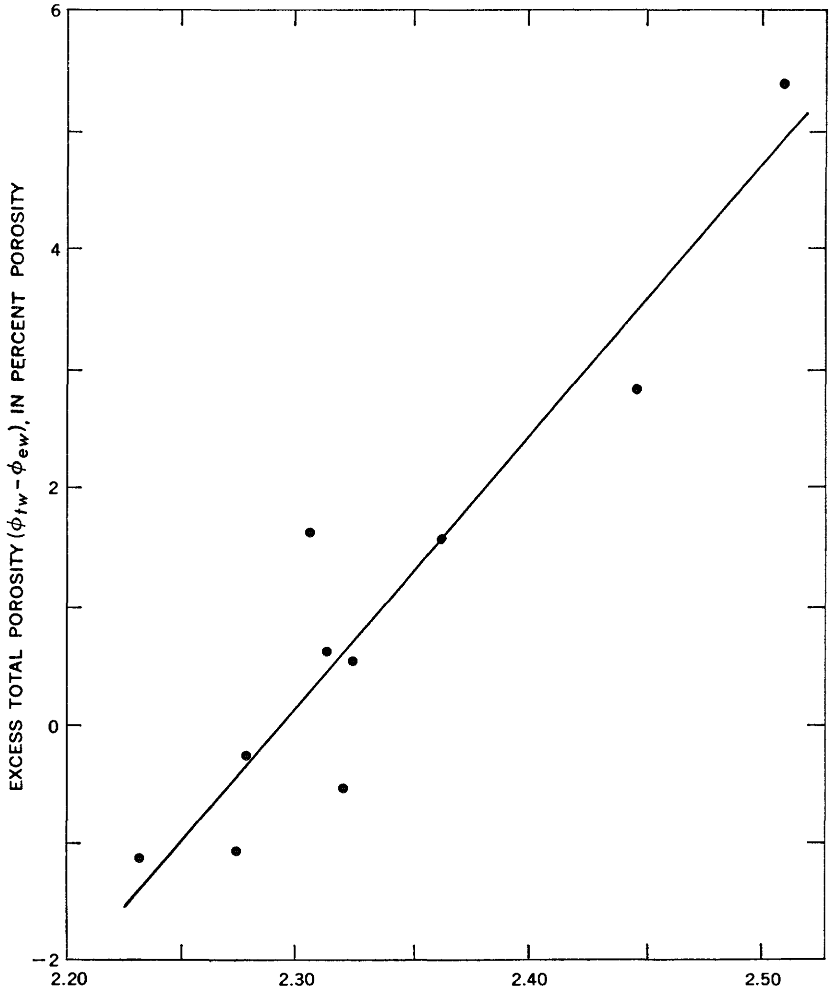

FIGURE 1.—Excess of total porosity of lapilli tuff (based on grain-powder density) over apparent porosity, plotted against grain-powder density. Both total porosity and apparent porosity are based on bulk volume determined by water displacement. After Manger (1965).

(Ezekiel and Fox, 1959, p. 130), shows that of 0.96 percent average excess total porosity for 10 specimens in table 3, an excess total porosity of 0.84 percent is due to the fact that on the average the grain-powder densities are greater than the grain densities of the whole specimens. Occluded pores, if present, do not include more than 0.12 percent of rock volume or 0.12 percent porosity. If in figure 1 the two points showing extremely high excesses of total porosity are omitted, the grain-powder densities of the remaining eight specimens are equally distributed about zero median excess total porosity. In this modification, the coefficient of determination shows that of 0.18 percent average excess total porosity, an excess total porosity of 0.10 percent is due to greater density of grain powders than of whole specimens. Thus, occluded pores or spuriously indicated occluded pores (because of adsorption of water by the grain powder or because of experimental error) do not constitute more than 0.12 percent porosity.

The small value of 0.12 percent excess porosity suggests that mean apparent porosity based on water-displacement bulk volume should approximate correct porosity. As noted in the section "Equality of total and apparent porosity," however, this suggestion is true only if water-displacement bulk volume yields the most acceptable value for bulk volume.

LARGER DIFFERENCE IN APPARENT-POROSITY THAN IN TOTAL-POROSITY VALUES

In table 3 apparent porosity based alternatively on water-displacement and mercury-displacement bulk volume shows a mean difference of 1.00 percent porosity. Total porosity alternatively based on corresponding bulk densities shows a mean difference of 0.98 percent porosity. The slightly greater apparent-porosity difference is to be expected according to the equations of table 1, whence the difference between apparent-porosity difference and total-porosity difference, for $V'_w > V'_m$, is $\gamma(a+b)V_g/V'_w$. The value of this fraction is small because the value of γ is small (in table 2 the average value of γ is 0.016); $a<1$; $V_g<1$, if a specimen shows any porosity; and, although the upper limit for b is not defined, it is very unlikely ever to be as great as V_g.

THE VALUE OF γ

The effect of method on values of bulk volume for lapilli tuff is indicated by the value of γ. In table 2, γ ranges from -0.005 to 0.030 and averages 0.016. The value of γ is expressed in terms of bulk-volume ratio in equation 8 as $V'_w/V'_m = 1+\gamma$, where V'_w and V'_m are respectively water-displacement and mercury-displacement bulk volume.

Bulk-volume ratios for the lapilli tuff from the Nevada Test Site in table 4 are compared with bulk-volume ratios of some other porous materials. For specimens of lapilli tuff having total porosity of about 38 percent, total-porosity difference increases from 0.83 percent porosity to 0.98 percent porosity as the ratio of water-displacement bulk volume to mercury-displacement bulk volume increases from 1.013 to 1.016. For Steinhoff and Mell's (1924) cubes of refractory material, having porosity of about 24 percent, a total-porosity difference of 1.4 percent porosity corresponds to a ratio for dimensioned to mercury-displacement bulk volume of 1.019. These relations suggest that for the lapilli tuff, a ratio of dimensioned to mercury-displacement bulk volume would increase the total-porosity difference of table 3 to about 0.98+2(0.98−0.83), or to 1.13 percent porosity. The corresponding increase in apparent-porosity difference would be to 0.83+2(1.00−0.83), or to 1.17 percent porosity. Because among observed values of bulk volume the dimensioned values usually are the greatest, maximum difference in porosity value for the lapilli tuff, as dependent upon the bulk-volume measurement, is probably not much more than 1 percent porosity.

TABLE 4.—*Ratios of bulk volume based on dimensioning, water displacement, and mercury displacement*

Author	Material	Total porosity (percent) based on bulk volume determined by—			Porosity difference (percent)	Bulk-volume ratio [1]
		Dimensioning	Water displacement	Mercury displacement		
Steinhoff and Mell (1924).	Porous refractory material [2].	25.0		23.6	1.4	[3] 1.019
Hartmann (1926)	Refractory brick [4]		25.5	24.6	.9	[3] 1.012
This study						
All specimens	Lapilli tuff [5]		38.65	37.67	.98	[6] 1.016
Without specimens 10 and 11			38.19	37.36	.83	[6] 1.013

[1] Equals $1+\gamma$ (see equation 8).
[2] 73 cubes, 2 cm along the edges.
[3] Computed from respective total porosities.
[4] 10 specimens of chamotte.
[5] 10 specimens, rounded and multiplaned, 3 cc to 8 cc in volume.
[6] Derived from measured bulk volumes.

The data of table 4 suggest that with decrease in porosity there is a persistence of much of the method-dependent difference between water-displacement and mercury-displacement values of bulk volume. For eight specimens of lapilli tuff having total porosity of about 38 percent, the bulk-volume ratio is 1.013 and $\gamma=0.013$. For Hartmann's (1926) specimens of refractory brick having total porosity of about 25 percent, the bulk-volume ratio is 1.012 and $\gamma=0.012$.

The texture of the surfaces of the refractory brick and of the lapilli tuff probably are different, but, with decreasing porosity, the volume of the previously mentioned surface pores likely decreases. The slight decrease in bulk-volume ratio that accompanies a large decrease in porosity from lapilli tuff to refractory brick suggests that many of the method-dependent differences between water-displacement and mercury-displacement bulk volumes persist to low porosities. According to table 1, in the vicinity of zero porosity, because of method-dependent differences of bulk-volume values, a difference in porosity of about γ is to be expected. For materials having the smooth surface texture of the specimens of lapilli tuff, the preceding relations suggest a difference of about 1 percent in porosity values in the vicinity of zero porosity because of differences in method-dependent values of bulk volume.

SUMMARY

Formulations of porosity differences show the effect of method-dependent values of bulk volume and the effect of adsorption, occluded pores, and other qualifying conditions on observed values of porosity. There is an increase in the magnitude of these effects, particularly of the method-dependent effect of bulk volume, as porosity decreases. Because of differences in bulk volumes measured by water displacement and by mercury displacement, observed values of porosity of lapilli tuff at about 38 percent porosity differ by an average of 1 percent porosity. Formulated differences of porosity and ratios of observed water-displacement to mercury-displacement bulk volumes suggest that, in the vicinity of zero porosity, materials having the surface texture of the lapilli tuff would show a difference of 1 percent porosity between porosity based on water-displacement and mercury-displacement values of bulk volume. For a substance having very low porosity, forced equality of porosity can be obtained by using the same pore volume for differently determined values of bulk volume, but this method ignores the fact that pore volume is determinable only as the excess of bulk volume over grain volume.

There seems to be no best method of bulk-volume measurement that is applicable to all porous substances. Mercury displacement usually furnishes minimum values and dimensioning usually furnishes maximum values for bulk volume. Because of the macroscopically smooth surfaces of the test specimens of lapilli tuff, determination of bulk volume by mercury displacement seems to be the most acceptable method for these specimens. Were the specimens coarse grained, the most acceptable method probably would be either that of water displacement or dimensioning. Because of its fugacity and high density, mercury may be expected to fill coarse-surface pores. As a result, for coarse-grained specimens the volume of displaced mercury would likely represent too small a bulk volume.

An excess of total over apparent porosity can result from factors other than the presence of occluded, or sealed-off, pores. For the lapilli tuff a seeming excess of 1 percent porosity is due to an average grain-powder density that is greater than the grain density of the test specimens. Occluded pores, if any are present, do not exceed 0.12 percent porosity.

Equality of total and apparent porosity where based on the same value of bulk volume indicates only that occluded pores are absent. It does not indicate that the best value of porosity has been obtained. Obtaining the best value of porosity depends upon obtaining the best value of bulk volume.

REFERENCES

Ezekiel, Mordecai, and Fox, K. A., 1959, Methods of correlation and regression analysis [3d ed.]: New York, John Wiley & Sons, Inc., 548 p.

Fancher, G. H., Lewis, J. A., and Barnes, K. B., 1933, Some physical characteristics of oil sands, *in* 3d Pennsylvania Mineral Industries Conf. Proc., Petroleum and Nat. Gas Sec.: Pennsylvania State Coll. Mineral Industries Expt. Sta. Bull. 12, p. 65–171.

Hartmann, F., 1926, Die Bestimmung des Raumgewichts und der Porosität feuerfester Steine nach dem Quecksilber-und dem Wasser-Verdrängungsverfahren: Fachausschüsse des Vereins deutscher Eisenhüttenleute Ber. 82, 9 p.

Hartmann, M. L., Westmont, O. B., and Morgan, S. F., 1926, The determination of the bulk and pore volumes of refractory materials: Am. Ceramic Soc. Jour., v. 9, p. 298–310.

Manger, G. E., 1965, The best value of porosity of lapilli tuff from the Nevada Test Site: U.S. Geol. Survey Prof. Paper 525–B, p. B146–B150.

Nutting, P. G., 1930, Physical analysis of oil sands: Am. Assoc. Petroleum Geologists Bull., v. 14, p. 1337–1349.

Steinhoff, E., and Mell, Maria, 1924, Porositätsbestimmungen an feuerfesten Steinen: Fachausschüsse des Vereins deutscher Eisenhüttenleute, Ber. 44, 6 p.