Pore Structure of Phosphate Rock and Triple Superphosphate

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Pore volumes and distributions of representative phosphate rocks and triple superphosphates were measured, to define the physical structure of such materials and relate it to chemical reactivity. Two experimental techniques, mercury porosimetry and evaluation of nitrogen desorption isotherms, provided coverage of the entire pore size range. Pore distribution is more important than total pore volume of phosphate rock. The pores of prime importance, less than 0.06 micron in diameter, are readily accessible to fluids reacting with the rock. In rock for electric furnace use, coarse as well as fine pores are necessary for efficient performance. In triple superphosphate, pores less than 0.06 micron are almost nonexistent; those from 0.06 to 5.0 microns are of greater extent and significance. Porosimeter depressurization measurements indicate that phosphate rock contains largely V-shaped or cylindrical pores, whereas triple superphosphate carries coarse "ink-bottle" pores.

THE PHYSICAL NATURE of fertilizer materials such as phosphate rock and superphosphate plays an important role in determining the rate of reaction of the materials under ordinary conditions of use—for example, in reactions with mineral acids, salt solutions, or soil solution. In fact, the reactivity under any specific condition depends directly upon the extent of surface exposed to the reacting fluid (8). Surface area measurements on fertilizer-grade phosphates (9) have shown that a large part of the total surface often lies inside the grains. Gross surface area is hence an insufficient index of the reactivity, inasmuch as the internal surface can be more accessible to the gas employed in surface area measurements than to reacting fluids. However, measurement of the extent and distribution of pores leading down into internal surfaces would define the interior physical structure of the material and allow more precise description of the true reacting surface.

To this end, pore properties have been determined on a group of phosphate rocks from different producing fields and a selection of triple superphosphates of current commerce.

Methods of Measurement

The complete pore spectrum may be pictured as encompassing a range of pore diameters from 100 microns (1×10^6 A.) down to about 10 A. Voids more than 100 microns in diameter are not measurable by normal techniques and are usually disregarded in pore studies; voids below 10 to 20 A. in diameter are of molecular dimensions and are of little importance in the aqueous reactions encountered in fertilizer systems.

Two methods of measuring pore volume and distribution, when used jointly, permit measurement of the complete pore spectrum. Mercury porosimetry, in which mercury is forced into pores by an applied pressure, is practicable for coarse macropores (200-A. diameter being the accepted demarcation between macro- and micropores). Micropores and fine macropores are more conveniently evaluated with use of low-temperature nitrogen desorption isotherms. Both methods have been applied to the fertilizer phosphates under test.

Mercury Porosimetry. When mercury is forced into a pore in a solid material, the pressure required to fill the pore completely is in inverse proportion to the size of the pore. The relationship, first pointed out by Washburn (13), is:

$$pr = -2\sigma \cos \Theta \qquad (1)$$

in which p is the pressure, r the pore radius, σ the surface tension of mercury, and Θ its angle of contact with the solid. Since σ and Θ are both constants, application of a known pressure yields the corresponding pore dimension. Precise measurement of changes in the volume of mercury as the pressure is increased thus indicates the volume of pores of a given size.

The porosimeter used in this work was a refined commercial instrument (American Instrument Co., Silver Spring, Md.), incorporating the same general features as the laboratory apparatus of Ritter and Drake (12). The unit is comprised of a vacuum system for evacuation of the sample prior to the introduction of mercury and for measurement of pore volumes at subatmospheric pressures, and a hydraulic pressure system, in which pressure is applied to the mercury surrounding the test specimen by means of a mechanical piston. The sample is contained in a portable calibrated glass penetrometer, and the changes in mercury volume are read on the scale of the penetrometer. A thick-walled glass port on the pressure chamber permits direct viewing of the penetrometer scale at above-atmospheric pressures.

Maximum pressure obtainable with this instrument is 3000 p.s.i., corresponding to a pore diameter of 600 A. Other porosimeter designs are known that reach much higher pressures; indeed, there is no theoretical limitation to the pressures obtainable. The 3000-p.s.i. unit was deemed satisfactory for present purposes, since the effective range of the nitrogen desorption method covers pores of 0- to 600-A. diameter, nicely abutting on the porosimeter range.

Nitrogen Desorption Method. Pore volumes were estimated by computations from nitrogen isotherms by a method described in detail by Barrett, Joyner, and Halenda (7). Conventional gas adsorption apparatus and techniques were employed, but calculations were based on the desorption branch of the low-temperature isotherm rather than the adsorption branch normally used in measurement of surface area. Results agree rather well with those of high-pressure mercury porosimetry (10). The principal drawback to the method is the length of time

required for each determination. Measurement of the isotherm normally requires 2 to 3 days and the subsequent calculations require another 2 days.

Character of Pore Volume Curves

The pore spectra of the test materials, as illustrated by the curves for two screened fractions of a typical phosphate rock in Figure 1, have a number of characteristics of general applicability and interest. Thus, the nitrogen isotherm measurements, which border on the end of the porosimeter range at a pore diameter of 0.06 micron (600 A.), form a curve having a slope that corresponds with the slope at the end of the porosimeter region, suggesting substantial agreement of the two methods. The two curves in the figure are virtually parallel for pores smaller than about 1 micron, denoting that the fine pore structure is uniform throughout the material, irrespective of particle size. The very sharp rise in apparent porosity of the finer 100- to 150-mesh material relates mainly to interparticle void space rather than particle porostiy. Considering the particles as spheres, the throats between 100- to 150-mesh particles could vary from 20 to 53 microns in diameter, depending upon the packing (7) The prismatic and sometimes even platelike particle shape of fertilizer phosphates undoubtedly leads to interparticle openings still smaller than 20 microns. Inasmuch as the steep portion of the curve lies almost entirely within the region above 20 microns, it is evident that pressure is required to force the mercury between the particles and that the apparent porosity is increased by the volume of the unoccupied voids. Since, however, 100- to 150-mesh particles (average diameter, 127 microns) cannot conceivably contain pores greater than 100 microns, it is possible to extrapolate from the point of inflection to zero slope at 100 microns, as shown by the broken line at the upper left of Figure 1, to define the change in particle pore volume. Comparison of this estimate to the curve for the coarser particles indicates logically that the latter carry a larger volume in wide pores. Extrapolations of this type were carried out with all fine-particle-size test samples in order to correct for interparticle voids.

Pore Structure of Phosphate Rock

Phosphate rocks included in the tests were among a group that had been previously characterized in a comparative study of the fertilizer value of rocks from different world-wide deposits (5) and represent the two extremes and an intermediate in the reactivity range, as indicated by both solubilization criteria and plant response. The cumulative
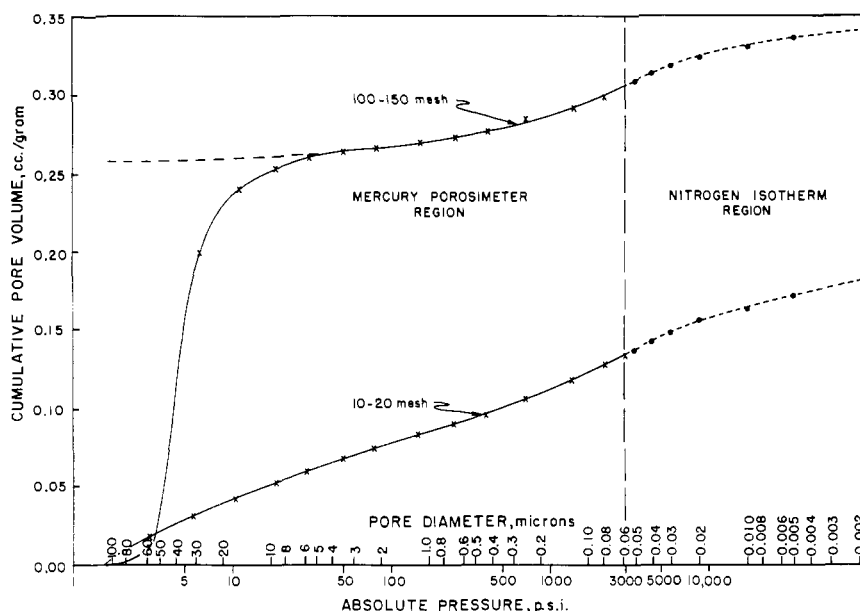

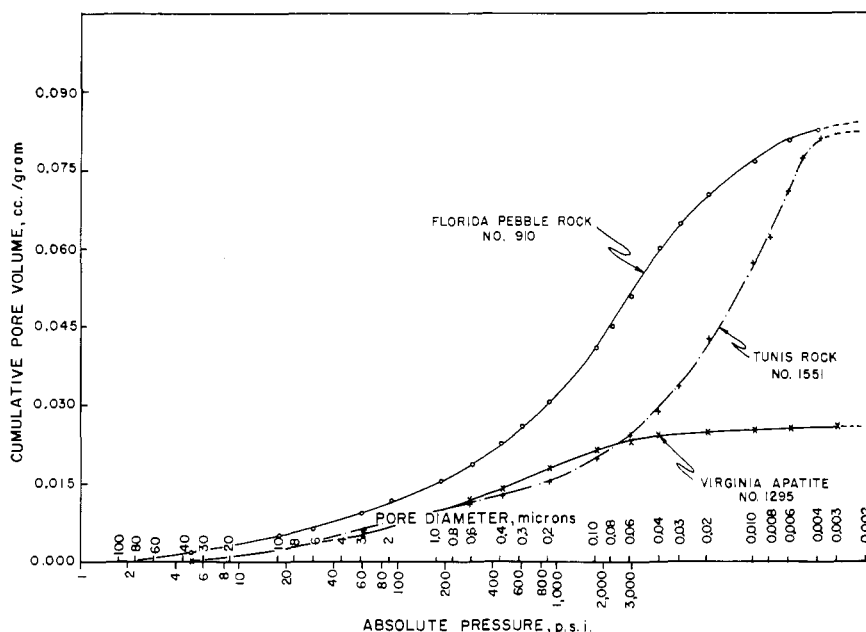
Figure 1. Pore spectra of a typical phosphate rock

Figure 2. Pore spectra of 100- to 150-mesh fractions of phosphate rocks

Table I. Pore Volume and Surface Area of Phosphate Rocks

Phosphate Rock	Relative Reactivity[a]	Surface Area[a], Sq. M./G.	Total Pore Volume, Cc./G.	% in Pores Finer than 600-A. Diameter
Tunis rock 1551	High	19.4	0.0885	66
Florida rock 910	Medium	10.3	0.0960	35
Virginia apatite 1295	Low	0.6	0.0310	10

[a] From Caro and Hill (5).

pore volume curves over the entire pore region are given for the three in Figure 2 and the pore volume distributions, obtained by differentiating the curves in Figure 2 and plotting the

logarithms of the derivatives, are shown in Figure 3. The data are corrected for interparticle voids.

The total pore volume of the Florida rock (intermediate reactivity) is slightly
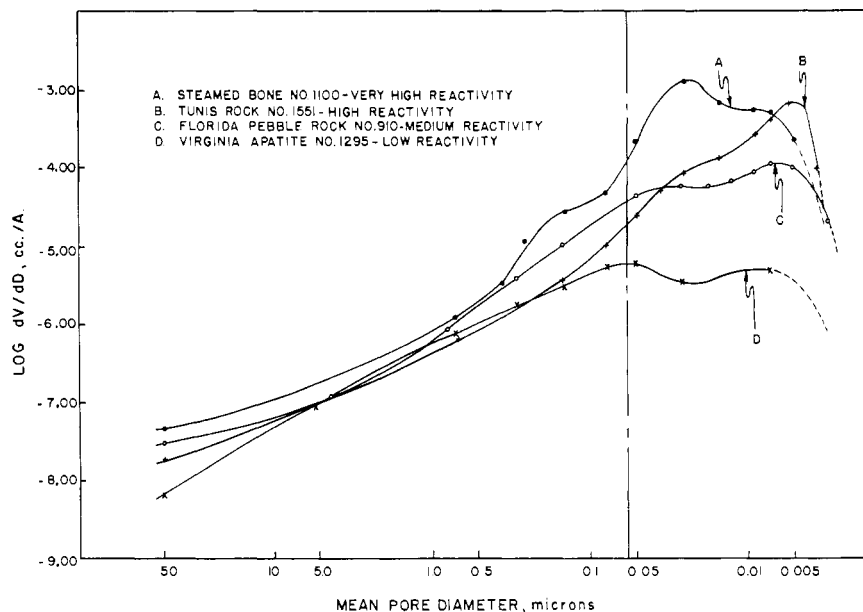
Figure 3. Pore volume distributions of phosphate rocks and steamed bone

A. STEAMED BONE NO.1100-VERY HIGH REACTIVITY
B. TUNIS ROCK NO.1551-HIGH REACTIVITY
C. FLORIDA PEBBLE ROCK NO.910-MEDIUM REACTIVITY
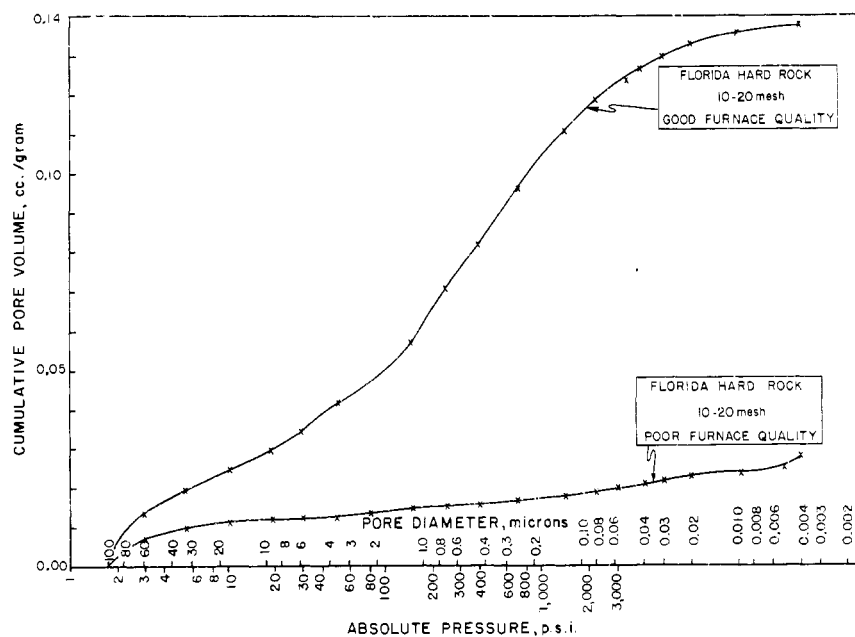D. VIRGINIA APATITE NO.1295-LOW REACTIVITY

Figure 4. Pore spectra of furnace rocks

greater than that of the Tunis rock (high reactivity), whereas the Virginia apatite (low reactivity) obviously contains fewer pores (Figure 2). The shapes of the first two curves differ, the Tunis rock having more fine pores and fewer coarse pores than the Florida rock. This results in unequal surface areas and contributes to the higher reactivity of the former. The pertinent figures are summarized in Table I. It is evident that the volume of fine pores (fine macropores as well as micropores) is the important criterion with respect to reactivity of phosphate rock, rather than the total pore volume.

A substantiating illustration is pro-vided in the pore distributions in Figure 3. Here, a very highly reactive steamed bone has been included with the test rocks to round out the comparison. The curves separate widely in the fine pore region, but converge at pore diameters larger than about 0.25 micron, suggesting that coarse pores have little or no influence on reactivity. This observation is borne out by the fact that the pore density of slightly reactive Virginia apatite is as high in the coarse region as that of the highly reactive Tunis rock.

The pore concentrations in the fine region, indicated by the height of the curves at the right side of Figure 3,

place phosphate rocks in the proper order with respect to reactivity. Interestingly enough, the peak pore diameters (the pore sizes in which the greatest pore volume is contained) do not fall into the same order. The steamed bone, bearing in general coarser pores than the phosphate rocks, is the more reactive material. It is very likely that two factors enter into this—bone has a higher intrinsic reactivity than rock; and the volume of coarser pores in the bone is large enough to compensate for the smaller volume of finer pores in the rocks.

Most of the pores in Tunis rock are only a few fold larger than molecular dimensions; on the other hand, most in the macrocrystalline Virginia apatite are larger by at least an order of magnitude, as might be expected. Because the reactivities of these materials have been ascertained in short-term solubilization tests (5), the data strongly suggest that even the very fine pores, those approaching molecular size, are entered by the reagent fluids in a short time, at least in 100- to 150-mesh particles. There thus appears to be little need, on purely mechanical grounds, to grind phosphate rocks beyond this particle size to derive the optimum benefit from the material, nor, apparently, will finer grinding materially aid crop response in field applications. In general, the experimental data indicate that material of high total porosity is not necessarily a desirable objective if one is seeking rock of optimum physical character; what is desirable is a rock having a large volume of pores less than 500 to 600 A. in diameter.

A special situation arises when a rock is to be used in the manufacture of elemental phosphorus in the electric furnace. Here, very large particle size is required for efficient performance and aggregated material is often used. High porosity is known to be desirable, coarse pores being of especial importance because of the magnitude of the pieces and the tendency toward coalescence in the furnace. Typical pore structures of two furnace rocks are shown in Figure 4. One had performed satisfactorily in the furnace; the other had not. The difference in porosity over the entire pore spectrum is evident and is undoubtedly the chief cause of the dissimilarity in performance. Pore measurements of this type can be helpful in laboratory evaluation of new diggings of furnace rock.

Pore Structure of Triple Superphosphate

A recent study in this laboratory of a number of commercial triple superphosphates has led to the conclusion that present-day products vary distinctly in granulation behavior, undoubtedly as a result of dissimilarity in physical char-

Table II. Volume and Distribution of Pores in 10- to 20-Mesh Fractions of Commercial Triple Superphosphates

Super-phosphate Product	Pore Volume in Pore Diameter Range, Cc./G.		Total Measured Pore Volume, Cc./G.
	5–100 μ	0.06–5 μ	
1	0.105	0.107	0.212
4	0.131	0.123	0.254
2	0.099	0.078	0.177
5	0.127	0.097	0.224
6	0.121	0.080	0.201
3	0.035	0.173	0.208
3ᵃ	0.062	0.125	0.187

ᵃ With particles fractured.

Table III. Mercury Retention in Fertilizer Materials on Depressurization to Near Zero Absolute Pressure

Material	Mercury Retained, % of Mercury Sorbed	
	+35-mesh material	−65-mesh material
Steamed bone 1100	29	3
Bone char 3189	80	90
Florida rock 910	74	5
Idaho rock 1253	90	91
Triple superphosphate		
7	33ᵃ	51
4	53ᵃ	66
6	72ᵃ	84

ᵃ Volumes retained. 0.138, 0.137, and 0.142 cc./g. in superphosphates 7, 4, and 6, respectively.
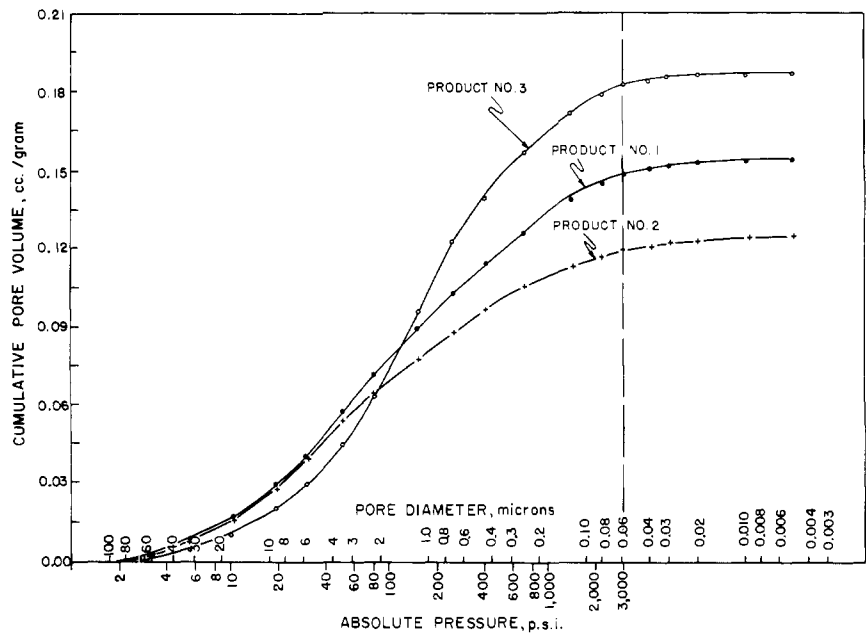
Figure 5. Pore spectra of synthetic particle-size mixes of commercial triple superphosphates
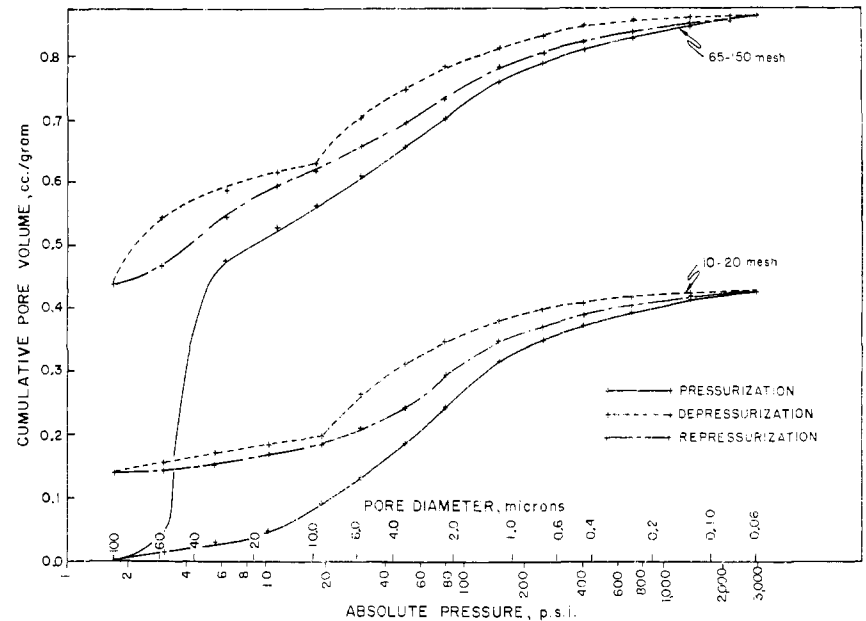
Figure 6. Hysteresis in the mercury porosimetry of a triple superphosphate

acter. A knowledge of extent and distribution of pores would appear to be helpful in elucidating the causes of the behavioral differences; hence pore measurements analogous to those described for phosphate rock have been carried out.

The cumulative pore volumes of three commercial triple superphosphates, corrected for interparticle voids, are shown in Figure 5. These materials were selected for test because they had exhibited obviously different characteristics in earlier studies of physical properties. The influence of particle size was eliminated by formulating in each case a mixture roughly approximating many run-of-pile products with respect to sizes of particles. These synthetic mixtures were comprised as follows:

10–20 mesh	15%
20–35	30
35–65	35
65–150	15
−150	5

The measurements reveal a pore structure in triple superphosphate that is entirely different from that in phosphate rock. The micropores and fine

macropores of the nitrogen desorption region, so prominent in rock, are extremely small in extent and exhibit a parallelism among all the test samples that implies that these pores contribute little to the performance qualities of the material. Similarly, the volume of coarse pores, those more than 5 microns in diameter, is almost the same in each of the materials. The difference between products thus lies in the intermediate pores, 0.06 to 5.0 microns in diameter.

Porosimeter measurements on 10- to 20-mesh fractions of six commercial triple superphosphates, including the

three of Figure 5, illustrate further points of interest (Table II). Inasmuch as the materials are listed together in groups of recognizably different physical character, it is evident that the total pore volume (column 4) is not a critical determinant of character. The volumes in intermediate pores (column 3), on the other hand, fall in line with the grouping. Product 3 is an unusual material having a hard, dense crust and a softer, more porous center. The crust contains mainly fine pores, through which mercury must be forced before the larger pores in the core can be reached. The apparent porosity is therefore low in the

coarse region and high in the fine. When the particles are fractured to expose the core (last item, Table II), the measured pore distribution shifts in the expected direction.

One triple superphosphate currently being manufactured with use of equipment normally employed for ordinary superphosphate (No. 7, Table III) exhibited an inordinately high porosity, total pore volume being 0.387 cc. per gram. Thus, including all measurements, the range of pore volume found in present-day commercial triple superphosphates is from 0.18 to 0.39 cc. per gram.

An important consideration with respect to the physical structure of triple superphosphate that cannot be neglected when porosity is discussed is the prevalence of large pits, troughs, or holes in the material. These cavities, formed in varying extent in the parent acidulation reaction, are of sufficient magnitude (over 0.1-mm. diameter) that mercury enters them even in the complete absence of pressure. They are not therefore treated as "pores" in the foregoing measurements, yet may be highly important to definition of the character of the material. No easily workable method is known for precise measurement of these cavities, although a microscopic thin-section technique offers promise (2).

Pore Shape Derived from Mercury Porosimetry

When the pressure is systematically released in the mercury porosimeter measurements, the depressurization curve does not follow the original pressurization curve and some of the mercury is retained in the sample even on complete removal of pressure. The phenomenon was also observed by Drake and Ritter (6), who attributed the action to the so-called "ink-bottle" shape of the pores. A somewhat more comprehensive investigation of this hysteresis and retention in the present fertilizer samples has been carried out, with illuminating results.

Curves illustrating hysteresis in two particle sizes of a commercial triple superphosphate, in general typifying the curves obtained with all the test superphosphates and phosphate rocks, are shown in Figure 6. The results are not unlike those obtained in capillary adsorption-desorption in microporous adsorbents, which has been thoroughly studied (3, 4). After the original pres-

surization, shown as the lowest in each triad of curves, cycles of removal and application of pressure are completely reversible, the curves following the upper two in each triad time after time.

The actual hysteresis—the deviation of the depressuring curve from the pressuring curve—is probably an additive effect of the difference between advancing and receding contact angles of mercury (14) and the irreversible chemisorption of the mercury on the pore walls, as manifested by the change in color of the sample upon pressurization (6). The hysteresis per se is hence of little value in pore studies. However, two other characteristics of the curves— the amount of mercury retained in the solid at near zero absolute pressure and the break in the depressuring curve at a pore diameter of about 10 microns— yield useful information.

The volume of mercury not emptying from the solid particles, expressed as a percentage of the volume originally taken in, is given in Table III for two particle sizes of a number of test materials. The bone products were included as reference materials, inasmuch as compact bone is known to be composed of open, essentially cylindrical canals (11).

Observations and Conclusions. Florida rock behaves like steamed bone, whereas Idaho rock parallels bone char. The pertinent relationship is seemingly the organic matter content (which interacts with and binds the mercury).

Phosphate rock has relatively few ink-bottle pores, as evidenced by the low retention in the fine particles when mercury binding (chemisorption) is absent. It also contains large internal chambers which retain mercury in the coarse particles.

In the superphosphates, the striking constancy of the volume of mercury retained, despite the fact that pore volumes, and hence surface areas, were of widely differing extent, constitutes strong evidence that chemisorption is insignificant and that the retention is a result of ink-bottle pore shapes. The constancy of retention, moreover, indicates that ink-bottling occurs primarily in the coarse pores, since all three test samples have almost constant coarse (> 10-micron diameter) porosity.

The transition observed in the depressuring curves at a pore diameter of about 10 microns (Figure 6) independently substantiates some of these conclusions. The break was very sharp in all superphosphates measured, notice-

able in the phosphate rocks, and nonexistent in the bone products. This implies that it is associated with closed, ink-bottle pores and points up the small proportion of the latter in phosphate rock. The curve to the right of the break (pores finer than 10 microns) may be interpreted as a smooth but retarded withdrawal of mercury from V-shaped or cylindrical pores. Then, at a pressure corresponding to 10-micron diameter and continuing down to lower pressures, some mercury is no longer withdrawn. Thus, it would seem that ink bottles, in which puddles of mercury would remain, occur only in coarse pores having throat diameters of 10 microns or more.

Literature Cited

(1) Barrett, E. P., Joyner, L. G., Halenda, P. P., J. Am. Chem. Soc. 73, 373–80 (1951).
(2) Bristow, R. L., Hardesty, J. O., Division of Fertilizer and Soil Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.
(3) Brunauer, S., "Adsorption of Gases and Vapors. Vol. I. Physical Adsorption," pp. 394, 408, Princeton Univ. Press, Princeton, N. J., 1945.
(4) Carman, P. C., J. Phys. Chem. 57, 56–64 (1953).
(5) Caro, J. H., Hill, W. L., J. Agr. Food Chem. 4, 684–7 (1956).
(6) Drake, L. C., Ritter, H. L., Ind. Eng. Chem., Anal. Ed. 17, 787–91 (1945).
(7) Graton, L. C., Fraser, H. J., J. Geol. 43, 785–909 (1935).
(8) Hill, W. L., in "Chemistry and Technology of Fertilizers," V. Sauchelli, ed., Reinhold, New York, 1960.
(9) Hill, W. L., Caro, J. H., Wieczorek, G. A., J. Agr. Food Chem. 2, 1273–7 (1954).
(10) Joyner, L. G., Barrett, E. P., Skold, R., J. Am. Chem. Soc. 73, 3155–8 (1951).
(11) McLean, F. C., Science 127, 451–6 (1958).
(12) Ritter, H. L., Drake, L. C., Ind. Eng. Chem., Anal. Ed. 17, 782–6 (1945).
(13) Washburn, E. W., Proc. Natl. Acad. Sci. 7, 115 (1921).
(14) Zsigmondy, R., Z. anorg. allgem. Chem. 71, 356 (1911).