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FERTILIZER TECHNOLOGY

Fineness of Commercial Florida Land Pebble and Other Phosphates Used in Superphosphate Manufacture

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Published collaborative studies were examined and screen analyses made on 16 samples of ground Florida land pebble to answer these questions: How reliable are routine screen analyses? How fine is the −200-mesh fraction? How coarse is the +100-mesh fraction? The precision of the −200-mesh determination, slightly less than half that of −100-mesh determination, corresponds with somewhat more than ±2% of the sample at 95% confidence. The average diameter of the −200-mesh (−74-micron) fraction is reduced by about one sixth in grinding from 50 to 85% finer than 200 mesh; the −50-micron fraction is not noticeably altered. The mean diameter of the +100-mesh fraction, excluding +32-mesh material, increases with the percentage of whole sample remaining on the 100-mesh sieve. The mean diameter of the −32-mesh fraction of the whole sample can be inferred from the percentage through the 200-mesh sieve to about 10 microns.

The current trend toward refinement in fertilizer processing brings a growing need for closer process control. Among demands of this kind is appraisal of the relative reactiveness of acidulation grades of phosphate rock. Looking to this need one views the trade specifications that call for certain percentages to pass the 100- and 200-mesh sieves and queries: How reliable are the determined percentages? How fine is the −200-mesh fraction? How coarse is the +100-mesh fraction? Responses to these questions are the primary concern of this paper. The quest for information on those issues, however, draws attention to other matters that merit brief treatment. Noteworthy among the latter are the importance ascribable to rock varieties as a factor in the variability of screen analysis, a comparison of two procedures for determining screen fractions, and the prediction of the average particle of a lot of rock from the determination of one of the commonly sought screen fractions.

Materials and Procedures

The data for the determination of the precision of screen analyses were derived from a published collaborative study of methods for mechanical analysis of phosphate rock (*5, 6*). Results from both screen analyses and complete mechanical analyses performed in the authors' laboratories on a recent collection of commercially ground Florida land pebble phosphates were used to determine average particle size of screen separates.

Collaborative Study. The study covered two years. In the first year (*5*) two lots of Florida land pebble were analyzed in triplicate by seven laboratories for the percentages passing the 100-mesh sieve and the 200-mesh sieve (wet). In the second year (*6*) nine laboratories, including the above seven, using the same procedure analyzed four varieties of rock, including a Florida soft phosphate, a Tennessee brown rock, a Wyoming rock, and a fresh portion from one of the lots of land pebble used the preceding year. Thus, 50 sets of triplicate determinations for each screen fraction were made on five rocks representing four varieties.

These five rocks are considered as a set typifying the ranges in physical character and analytical difficulty encountered in domestic ground phosphate rock. Grade and variety were not considered. This is desirable because the emphasis is on variability of determining two common screen fractions rather than one fineness per se. This course seems permissible because grade and variety can be factors only in so far as they influence the physical homogeneity and screenability of the rock.

Standard deviations of individual laboratory means were calculated and classified into frequency distributions, in order to evaluate laboratory performance on the basis of precision. Differences among laboratories were handled in a similar manner to show laboratory performance with respect to accuracy.

Table I. Florida Land Pebble Phosphates Used in Physical Composition Study

Lot No.	Grade BPL, %	Grade P_2O_5, %	Amount Passing 200-Mesh Sieve[a], %
3372	68	31.0	50
3373	68	31.1	85
3374	70	32.1	70
3375	72	33.0	50
3378	72	33.1	55–60
3379	72.5	33.2	70–75
3156	73	33.4	[b]
3157	73	33.5	[b]
3155	73.5	33.7	80–85
3301[c]	75	34.5	50
3376	75	34.3	60
3381	75	34.5	70–75
3377	75	34.3	72
3380	76	34.6	55–60
3302[d]	76	34.7	85
3359–b	77.5	35.5	60–65

[a] Producer's specification.
[b] Special preparation used by Fox *et al.* (*4*).
[c] Association of Florida Phosphate Mining Chemists' check sample 30; used by Haven and Jacob (*5*).
[d] Association of Florida Phosphate Mining Chemists' check sample 31; used by Haven and Jacob (*5*) and by Jacob and Hoffman (*6*).

Table II. Mechanical Composition of Florida Land Pebble Phosphates by Soil Survey Method of Analysis

Lot No.	Percentage Smaller Than 2 μ	20 μ	50 μ	105 μ	177 μ	250 μ	500 μ	1000 μ
3375	6.4	18.8	40.0	65.2	82.8	90.4	96.6	99.8
3378	7.8	20.8	41.3	66.3	80.7	88.3	94.6	98.6
3301	7.3	20.2	42.1	65.7	83.8	95.3	99.6	100.0
3372	6.2	20.0	43.2	70.8	84.6	92.1	97.5	99.7
3380	6.4	19.9	43.0	73.5	90.4	97.1	99.6	100.0
3359-b	6.9	26.4	47.7	72.5	90.1	96.4	99.3	100.0
3376	5.9	20.2	44.7	72.2	89.6	96.0	99.2	99.9
3374	6.5	25.4	52.4	79.3	91.1	96.2	99.0	99.9
3381	6.7	22.4	49.7	82.7	95.6	98.7	99.8	100.0
3157	7.6	31.3	55.1	83.3	98.4	99.9	100.0	...
3377	6.5	24.1	55.6	85.9	96.5	99.0	99.8	100.0
3379	8.3	26.1	53.0	83.6	95.6	98.7	99.8	100.0
3156	10.1	36.1	68.5	92.8	98.4	99.5	99.9	100.0
3373	10.0	35.3	61.7	88.6	99.6	99.9	100.0	...
3155	9.9	33.1	68.1	92.0	97.4	99.1	99.7	99.9
3302	7.8	38.7	71.2	95.0	99.4	99.9	100.0	...

Table III. Range of Fineness and Experimental Precision for Ground Phosphate Rock[a]

Rock Variety	Range of % Passing Sieve	Av. Std. Dev. of Means (within Laboratories)	Av. Differences between Single- and 7-Laboratory Means (among Laboratories)
	100-Mesh Sieve		
Pebble, 23 obs.	76.3–98.4	0.11	0.40
Other, 27 obs.	95.5–99.5	0.10	0.31
	200-Mesh Sieve		
Pebble, 23 obs.	54.4–87.2	0.30	0.58
Other, 27 obs.	80.1–93.5	0.24	1.01

[a] 2 lots of Florida land pebble and 1 each of Florida soft phosphate, Tennessee brown rock, and Wyoming phosphate.

Combined analyses of variance were made to obtain estimates of the within-laboratory and laboratory-to-laboratory components of variance within the four varieties of rock. These components were calculated for both the −100- and −200-mesh fractions. Estimates were obtained of the expected variance of the means for various schemes of collaborative analyses differing in both the number of determinations and the number of laboratories by combining the two components of variance in the following formula:

$$\sigma_x^2 = \frac{\sigma_l^2}{l} + \frac{\sigma_d^2}{ld}$$

where σ_x is the expected variance, σ_l^2 is the estimated component for laboratories on a single lot, σ_d^2 the estimated component for determinations in a single laboratory, and l and d, respectively, are the number of laboratories and the number of determinations per laboratory. Confidence limits were calculated by multiplying the expected variance by the appropriate t value.

Physical Composition. The 16 lots of Florida land pebble described in Table I were analyzed by the official method of the Association of Official Agricultural Chemists for mechanical analysis of phosphate rock (*6*) and also by the Soil Survey Laboratory procedure for the mechanical analysis of soil (*7*). The first procedure, used in the collaborative study, involves wet-sieving a sample of the lot on a 200-mesh sieve followed by dry-sieving the retained fraction with the use of the 100- and 200-mesh sieves. In the second procedure the sample is first split at the 50-micron size by dispersing it in water with the use of agitation and sodium hexametaphosphate as a dispersant, pouring the suspension through the sieve, and washing the retained fraction thoroughly with water. The coarse material is fractionated by dry-sieving, whereas the filtered suspension is analyzed by sedimentation and pipetting. The particle size distributions of Florida land pebble rocks from single determinations of the respective size classes by the Soil Survey method are given in Table II. Plots (not shown in figures) of these accumulative results were used to interpolate on the chord the percentages smaller than 149 and 74 microns, corresponding with the openings of standard 100- and 200-mesh sieves, respectively.

Particle Size of Screen Separates. The fineness, or coarseness, of a screen fraction is gaged by the diameter of the particles in it. Values for this index of fineness were calculated from the particle size distributions given in Table II. Accordingly, the mean weight diameters of screen fractions having special interest were obtained by summing the products of the average diameters and weight fraction of the various size classes and dividing by the sum of the weight fractions.

Table IV. Precision of Screen Analyses in Successive Years on One Lot of Florida Land Pebble

Lab. No.	Standard Deviation of Laboratory Mean: −100-Mesh Fraction 1955	−100-Mesh Fraction 1956	−200-Mesh Fraction 1955	−200-Mesh Fraction 1956
1	0.09	0.09	0.58	0.54
2	0.08	0.12	0.12	0.05
3	0.08	0.08	0.08	0.24
4	0.05	0.03	0.66	0.21
5	0.05	0.00	0.12	0.04
6	0.05	0.16	0.57	0.17
7	0.13	0.03	0.12	0.40

Collaborative Study Results

Variability in Collaborative Study. The over-all variability of results on Florida land pebble and that for the other three rock varieties are shown in Table III. The range of fineness is considerably greater for the Florida land pebble than for the other phosphates. However, the variations within a laboratory determination are approximately the same for a given screen fraction. The differences between single- and seven-laboratory means show much more variation among laboratories than between determinations within a laboratory.

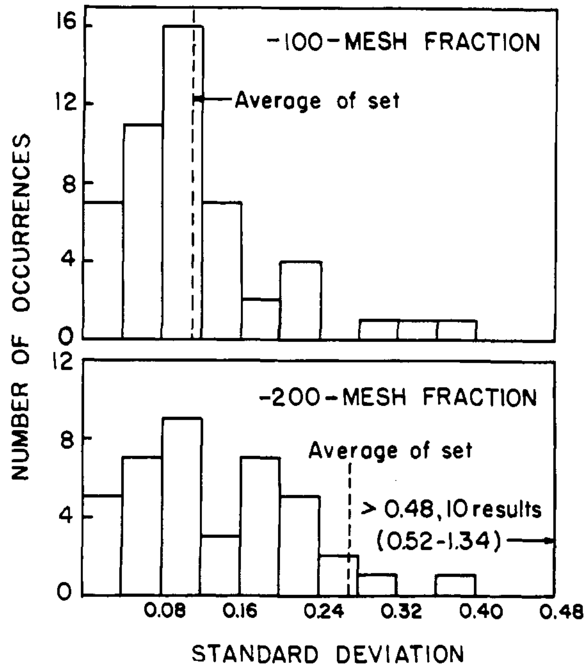

Figure 1. Frequency distribution of standard deviations of 50 laboratory means of triplicate determinations of −100- and −200-mesh fractions

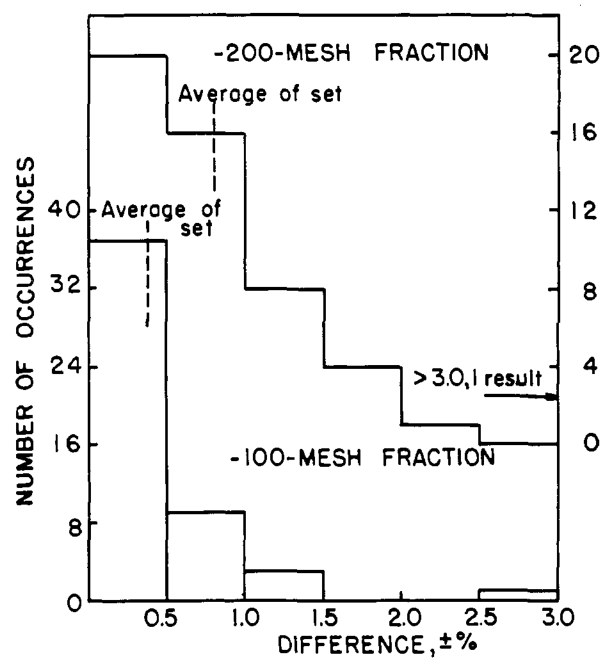

Figure 2. Frequency distribution of 50 differences between single- and seven-laboratory means of triplicate determinations of −100- and −200-mesh fractions

Precision of Determinations. Consistency of laboratory performance as regards agreement of triplicate determinations is illustrated in Table IV by standard deviations of laboratory means obtained in successive years on a lot of Florida land pebble (No. 3302, Table I). The precision is noticeably lower for the −200-mesh fraction and varies among laboratories and between years.

The observed frequency of standard deviations of laboratory means for all lots of rock used in the collaborative study that lie within class intervals of 0.04 is depicted in Figure 1. In the case of the −200-mesh fraction 10 of the 50 results lie off the figure—a circumstance responsible for the average of the set falling well above the range of highest frequency.

Class intervals, D, of 0.5% confidence limits in terms of fraction of sample passing a given screen were established. The ranges of standard deviations that would result in determinations of the specified precision were calculated. The 50 standard deviations for both the −100-mesh and −200-mesh fractions were then tabulated according to these calculated ranges (Table V). All 50 triplicate determinations of the −100-mesh fraction had standard deviations that would give confidence limits of less than ±1%. Similarly, 44 of the determinations of the −200-mesh fraction lie in the first two classes. The six larger standard deviations were distributed among laboratories and rocks as follows: Laboratory 1, one each to pebble and Wyoming; Laboratory 4, two to pebble; Laboratory 6, one each to Tennessee and Wyoming.

Table V. Frequency Distributions of Standard Deviations by Classes of Precision

Range of Precision, D, ± %	Calcd. Range of Std. Dev., s[a]	Obsd. Frequency of Std. Dev. −100-mesh fraction	Obsd. Frequency of Std. Dev. −200-mesh fraction
0.5	0.295	47	38
0.5 to 1.0	0.295 to 0.590	3	6
1.0 to 1.5	0.590 to 0.886	0	4
1.5 to 2.0	0.886 to 1.181	0	0
2.0	1.181	0	2

[a] Range that would result in range of precision (95% confidence) specified in 1st column; derived from relationship, $D = t(2s^2/n)^{1/2}$, in form $s = 0.5904\ D$, in which $n = 3$ and $t = 4.303$ from Student's t distribution for 2 degrees of freedom.

Table VI. Accuracy of Screen Analyses in Successive Years on One Lot of Florida Land Pebble

Lab. No.	Difference between Single- and 7-Laboratory Means: −100-Mesh Fraction 1955	−100-Mesh Fraction 1956	−200-Mesh Fraction 1955	−200-Mesh Fraction 1956
1	0.00	0.11	0.12	0.92
2	0.03	0.05	−0.48	−0.15
3	−0.07	0.21	0.59	−0.15
4	−0.14	0.15	−0.84	−1.81
5	0.36	−0.42	1.02	−0.68
6	0.00	0.08	0.29	1.19
7	−0.20	−0.19	−0.71	0.69
Mean of 7 laboratories	98.47	98.42	87.21	87.18
Std. error of mean	0.18	0.22	0.70	1.04

Accuracy of Determinations. Consistency of laboratory performance as regards agreement with the all-collaborator mean is illustrated in Table VI by differences between single-laboratory and seven-laboratory means obtained in successive years in Florida land rock No. 3302 (Table I). The differences for the −200-mesh fraction are not only the larger but also show the wider variation.

The observed frequency of differences for all lots of rock used in the collaborative study that lie within class intervals of 0.5% is depicted in Figure 2. In the case of the −100-mesh fraction 46 of the 50 differences were within ±1%. The corresponding figure for the −200-

mesh fraction is 36. These frequencies, though somewhat lower, follow the order exhibited by the standard deviations of laboratory means. The 14 differences that were greater than ±1% were divided nearly equally among laboratories 2 to 9—four pebble, six Wyoming, two Tennessee, and two Florida soft phosphate. With the exception of one very high value, the differences range up to 2.5%, which is something less than the desirable accuracy of triplicate determinations. Perhaps the results of phosphate rock analyses by different laboratories could be brought into closer agreement by the use of methods developed in bone char studies for sieve calibration (*3*) and determination of the sieving end point (*2*).

Expected Reliability of Screen Analyses. Expected confidence limits for screen analysis are given in Table VII. Values are shown for the limits of means of one to three determinations per laboratory in one to seven laboratories. As would be anticipated, the expected confidence limits are much less for the −100-mesh fraction than the corresponding limits for the −200-mesh fraction.

Table VII. Expected Confidence Limits (95%) for Screen Analysis of Phosphate Rock

No. of Detns. in Laboratory	Confidence Limits, ±% of Sample			
	1 lab.	*2 lab.*	*3 lab.*	*7 lab.*
	−100-Mesh Fraction			
1	1.30	0.918	0.751	0.491
2	1.27	0.900	0.735	0.481
3	1.26	0.894	0.731	0.477
	−200-Mesh Fraction			
1	2.60	1.84	1.50	0.984
2	2.51	1.78	1.45	0.948
3	2.48	1.75	1.43	0.936

However, the −200-mesh fraction, which the trade considers the critical index of fineness of grind, possesses the principal interest at the moment. According to the table, a single determination of this fraction in one laboratory can be expected to lie within ±2.60% of the true mean 95% of the time. With triplicate determinations in one laboratory this figure can be lowered to ±2.48%—a trifling reduction. On the other hand, the mean of single determinations in three laboratories would be expected to lie within ±1.50% of the true mean. If it be desired to attain a confidence limit of less than ±1% for the −200-mesh fraction, single determinations in at least seven laboratories will be required. These findings illustrate the large laboratory-to-laboratory variation in comparison with the rather small variation among determinations within a laboratory.

Physical Composition

Comparison of Results by Two Procedures. The interpolated results present an opportunity for an interesting comparison of the performances of the AOAC and Soil Survey procedures. The results are given in Table VIII, the arrangement being in increasing order of the −200-mesh fraction found by the official AOAC procedure. The differences between corresponding results occur with both signs, and the absolute values are generally smaller for the −100-mesh fraction, where they range from 0.1 to 4.2, mostly all below the level of statistical significance. The differences for the −200-mesh fraction range from 0.3 to 5.3 with the exception of the one significant difference of 7.8. Triplicate determinations of the two size fractions made days apart by the two methods on Florida land pebble rocks 3372 and 3302 (Table I) mark the Soil Survey results with the higher precision. The standard deviations of the four procedure means ranged from 0.05 to 0.12 by the Soil Survey method in comparison with 0.05 to 0.40 for the official AOAC method. However, the differences between paired procedure means followed the pattern for single determinations (Table VIII), being 0.03 and 0.30 for the coarse fractions and 2.47 and −1.70 for the fine fractions.

Table VIII. Single Determinations of −100- and −200-Mesh Fractions

Lot No.	Percentage Finer Than 100 Mesh: Soil Survey proc.	Official screen proc.	Diff.[a]	Percentage Finer Than 200 Mesh: Soil Survey proc.	Official screen proc.	Diff.[a]
3375	76.5	74.5	2.0	53.1	51.9	1.7
3378	75.5	74.7	0.8	54.5	52.7	1.8
3301	77.2	75.2	2.0	54.5	52.8	1.7
3372	79.8	78.6	1.2	57.7	57.0	0.7
3380	84.2	83.3	0.9	59.2	58.0	1.2
3359-b	84.1	79.9	4.2	60.7	59.8	0.9
3376	83.5	80.5	3.0	59.0	61.4	−2.4
3374	87.0	84.7	2.3	66.6	66.3	0.3
3381	91.1	91.3	−0.2	67.4	68.6	−1.2
3157	93.0	90.2	2.8	69.1	68.6	0.5
3377	92.6	89.8	2.8	70.6	68.7	1.9
3379	91.5	89.7	1.8	69.5	69.5	0.0
3156	96.5	97.0	−0.5	81.4	73.6	7.8
3373	96.0	92.6	3.4	75.9	81.2	−5.3
3155	95.5	95.3	0.2	80.7	83.5	−2.8
3302	97.9	98.2	−0.3	83.9	86.8	−2.9

[a] Minus sign indicates result by Soil Survey procedure was smaller. Use of interaction between methods and samples as experimental variance yields 3.00 and 6.17 as least significant differences (with 95% confidence) between results by two procedures for two size fractions, respectively.

Average Particle Size of Screen Separates. Answers to the last two of the three major questions raised in the introductory paragraph are provided by the average particle sizes of the appropriate screen fractions of rocks ground to different degrees of fineness.

Fraction Finer than 200 Mesh. The dependence of the mean particle size of the −200-mesh fraction on its weight per cent of the lot is depicted in Figure 3,*A*. The mean diameters range from about 36 to 28 microns and fall along a downward sloping line, drawn by inspection, which indicates a reduction in mean particle size as the rock is ground to show larger and larger percentages finer than 200 mesh. For example, milling a rock from 40 to 80% finer than this sieve would be expected to lower the average particle size of this separate about 7 microns. On the other hand, the mean size of the −50-micron fraction removed from lots having the fineness shown was not appreciably affected by fine grinding (Figure 3,*B*). Hence, it appears that in current mill practice the grinding process operates only on particles coarser than 50 microns.

Fraction Coarser Than 100 Mesh. Necessary definition of the size range +100-mesh fraction requires a stated upper limit of the range. It happens that a few of the test rocks were 100% finer than 500 microns (Table II), whereas the others contained 0.1 to 5.4% of coarser material. A reasonable and practical upper limit would thus appear to be 500 microns, or 32 mesh. Accordingly, the mean weight diameters of the 32- to 100-mesh fractions are plotted against the percentage of the lot retained on the 100-mesh sieve in Figure 4. The scatter of the experimental points is markedly greater here than in the case of the −200-mesh fraction. Nevertheless, the results show an obvious trend to larger average particle diameters with increase in the amount of material retained on the 100-mesh sieve. The average particle size ranges from about 180 to nearly 260 microns.

An opinion voiced in the past, and presumably based on the extreme hardness of the quartz constituent, regards the +100-mesh fraction as being silica for the most part. This view is not valid for ground rock marketed at

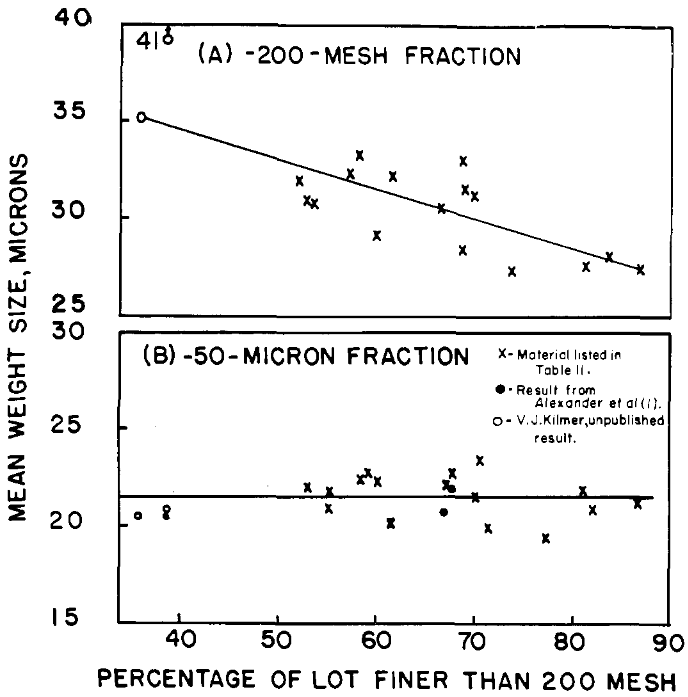

Figure 3. Average particle diameter of —200-mesh and —50-micron fractions of Florida land pebble

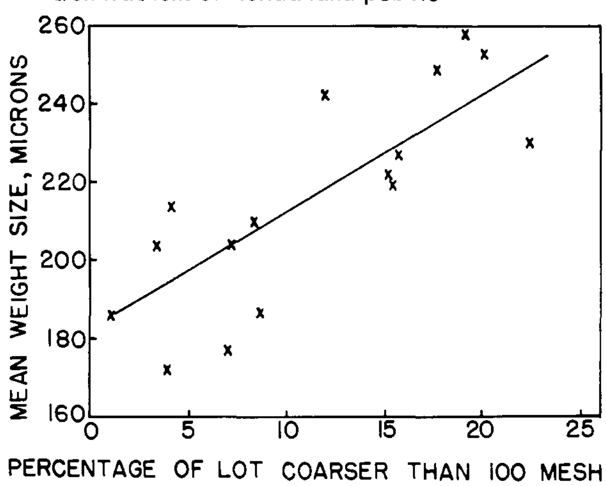

Figure 4. Average particle diameter of 32- to 100-mesh fractions of Florida land pebble

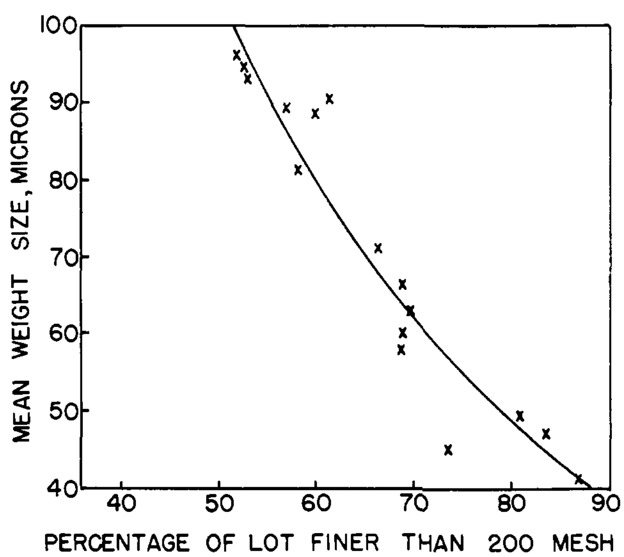

Figure 5. Average particle diameter of —32-mesh lots of Florida land pebble

the present time. The +100-mesh fractions of the test rocks showed P_2O_5 contents that ranged from 28.4% for a rock containing 68% BPL to 34.5% for one containing 77.5% BPL.

Average Particle Size of Lot. The mean weight diameters of the test rocks, excluding from the calculation any +32-mesh particles, are plotted in Figure 5 with respect to the percentage of the lot finer than 200 mesh. According to a least squares treatment, the results follow a curvilinear relationship significantly better than a linear one at 90% confidence. The mean size decreases with finer grinding and ranges from about 100 microns for 50% finer than 200 mesh down to about 48 microns for 80% finer than 200 mesh. Thus, with milling techniques currently used in the phosphate rock industry in Florida, grinding from the coarse extreme of the usual fineness range to the other extreme approximately halves the particle size.

Applications

The data on the expected reliability of screen analyses and the average particle size of screen separates can be applied by the producers of ground phosphate rock toward improving their process control. This information can also be used by the superphosphate producers for improved control of their acidulation processes.

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