

Heavy applications of nitrogenous fertilizer to alfalfa and trefoil did not change greatly their per cent protein. However, per cent nitrate in alfalfa was increased while it was changed very little in trefoil.

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FERTILIZER RAW MATERIALS

Reactivity Range of Nonblended Florida Pebble Phosphate

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Phosphate rocks from different locations within the Florida fields showed small differences with respect to chemical composition, but rather large differences in physical properties. The rates of reaction with acid exhibited by the specimens appeared to be associated more with chemical than with physical characteristics. Consequently, the observed differences in reaction rates were considerably smaller than the differences between Florida rocks and those from other geographic deposits. A 35-year-old Florida rock used to calibrate a general scale of rock reactivity proved to be somewhat more reactive than the general run of rock now being mined in Florida.

PHOSPHATE rocks from different geographic deposits vary widely in speed of reaction with acid. Differences in reactivities of commercial rocks have long been recognized by superphosphate manufacturers, though only recently has attention been given to the development of a scale of reactivity as a means of classifying phosphate from different sources (6). This scale was defined in terms of the relative reactivities of available specimens of rock from several fields. Although these specimens represented points on the reactivity scale, they did not necessarily typify specific varieties of rock, because rock from the same producing field may vary considerably.

The type specimen of Florida land pebble was found to have an intermediate reactivity. Since this variety of rock supplies 75% of the phosphorus in domestic rock sold or used by the producers, a survey was undertaken to determine its range in reactivity. The findings are summarized in this paper.

Selection and Procurement of Test Samples

The land pebble phosphate region in Florida, located in the west-central part of the state (Figure 1), is divided on the

basis of phosphorus content into a northern, high-grade area and a southern, lower grade area (4). Current commercial mining activity is confined to the northern district, in Hillsborough and Polk Counties. This territory is subdivided into smaller areas containing rock deposits recognized by the mining community as differing in hardness, color, and grade from those in adjoining areas. Thus, five mining districts may be distinguished: (1) a small region east of Bartow, containing very soft ore; (2) a larger area east of Lakeland, comprised of moderately soft, high-grade ore appearing as mixed black and white pebbles; (3) another region of the same type of rock but of medium grade, west of Mulberry; (4) an area extending south from Mulberry, containing hard, dominantly black pebble, of medium to low grade; and (5) a large area extending from the west of Bartow southeast to Fort Meade along the Peace River and containing hard, yellowish rock, chiefly of concentrate size.

To provide general coverage of the Florida field, one mining company in each district was asked to furnish test samples in three size classifications, corresponding as closely as possible to coarse pebble, fine pebble, and flotation

concentrates. Samples were to be from plant output before the blending of grades that is normally practiced in commerce to provide products of specified grade. The materials submitted and judged by producers to be typical of each variety of rock are listed in Table I and their major chemical composition is shown in Table II. Only one size of rock was received from district 1 because the producer contacted is now out of commercial production in that area.

To eliminate particle size as a variable, all samples were ground and/or screened to 100 to 150 mesh prior to testing.

Scope of Measurements

The survey includes measurement of those properties of a rock that are considered to influence its reactivity—carbonate, fluorine, iron, and aluminum contents, calcium-phosphorus ratio, pore size distribution, and surface area (2, 6, 9)—as well as estimation of the relative reactivity itself by known techniques: measurement of phosphorus solubility in solutions of neutral ammonium citrate, citric acid, and phosphoric acid (3, 8). The rate of solubilization in phosphoric acid is related directly to the manufacture of triple superphosphate; the analogous rate in sulfuric acid as in

normal superphosphate manufacture has not been investigated sufficiently for inclusion in this report, although it is presumably an equally valid index of reactivity.

Experimental Methods

Chemical Assays. Phosphorus, fluorine, and carbon dioxide were determined by official AOAC procedures. Other methods included: EDTA titration for calcium after removal of phosphorus with ion exchange resin; potassium dichromate titration for iron; photometric determination of aluminum, based on formation of a complex with aluminon; and bound carbonate determination by the official method for carbon dioxide, but carried out on the residue obtained after dissolution of free carbonate (calcite) in a solution of triammonium citrate (70).

Solubility in Citrate and Citric Acid. The solubility in neutral ammonium citrate solution was measured by the official AOAC procedure. Solubility in 2% citric acid solution was found by shaking 1 gram of sample in 100 ml. of the acid for 30 minutes at 24° C., filtering, and determining the dissolved phosphorus.

Rate of Reaction with Phosphoric Acid. A method for characterizing phosphate rocks by measuring their rate of reaction with dilute phosphoric acid (8) was modified as follows. A 1-gram portion of rock was made to react with 5 ml. of 30% H₃PO₄ (a large excess of acid) for 10 minutes. The reacted mixture was rapidly filtered, the residue copiously washed with water, and the citrate-insoluble phosphorus content determined. The soluble phosphorus was then expressed as a fraction of the total phosphorus in the material to obtain the rate index.

Physical Properties. Surface areas were determined by the BET nitrogen adsorption method (7). Pore volumes and pore size distributions were obtained by mercury porosimetry for pores coarser than 600-A. diameter and by nitrogen desorption for finer pores (2). True density, the density of the solid material of the rock, was determined by displacement of helium; particle density, the density of the rock particles including interior voids, was measured by displacement of mercury.

Inferred Reactivity of Test Rocks

Derived from Bound Carbonate Content. In the earlier study of phosphate rocks of different geographic origins (3), the carbonate content contained within the apatite crystal (bound carbonate) proved to be a valuable index of fertilizing quality of the materials when compared with plant yields in a greenhouse experiment. It is, therefore, an indirect indicator of relative reactivity. The Florida rocks in the present investigation contain little free carbonate (Table II, footnote); hence total carbonate content suffices as the index.

Table I. Source and Size Classification of Florida Phosphate Rocks

Lot No.	District	Producer's Designation	Particle Size, Mesh
3422	2	Coarse pebble	+4
3423	2	Fine pebble	4-16
3424	2	Flotation concentrate	16-150
3425	5	Coarse pebble	4-16
3426	5	Agglomerate concentrate	16-35
3427	5	Flotation concentrate	35-150
3428	3	Coarse pebble	+8
3429	3	Fine pebble	8-20
3430	3	Flotation concentrate	20-150
3431	4	Coarse rock	+4
3432	4	Regular rock	4-16
3433	4	Concentrate	16-35
3434	1	Pebble	+16

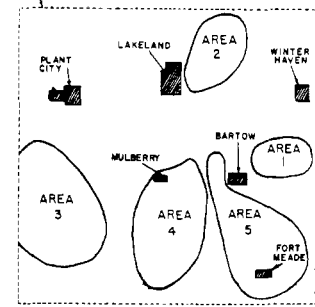
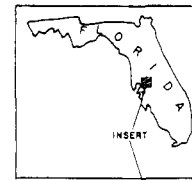


Figure 1. Florida phosphate field.

Table II. Chemical Composition of 100- to 150-Mesh Fractions of Florida Phosphate Rocks

Lot No.	P (BPL), %	Ca, %	Ca/P, Wt. Ratio	Fe ₂ O ₃ , %	Al ₂ O ₃ , %	F, %	CO ₂ ^a , %
3422	13.0 (65)	30.4	2.34	0.8	0.8	3.5	4.0
3423	13.6 (68)	32.7	2.40	1.0	0.7	3.6	3.9
3424	14.8 (74)	34.7	2.34	1.4	0.9	3.7	3.6
3425	14.1 (71)	31.9	2.26	1.8	1.4	3.7	2.4
3426	14.3 (72)	32.4	2.27	1.5	1.1	3.6	2.4
3427	15.0 (75)	33.9	2.26	1.3	1.7	3.8	2.7
3428	14.8 (74)	32.4	2.19	0.9	2.2	3.5	2.1
3429	14.4 (72)	32.4	2.25	1.0	1.1	3.8	2.0
3430	15.5 (77)	35.2	2.27	1.3	1.2	3.9	2.4
3431	12.7 (64)	30.6	2.41	0.8	1.5	3.4	4.0
3432	14.0 (70)	33.2	2.37	0.7	1.2	4.0	3.6
3433	13.7 (68)	32.9	2.40	0.6	1.2	3.8	3.8
3434	14.6 (73)	34.4	2.36	0.5	0.9	4.3	2.9

^a CO₂ as free calcite was 0.18% in No. 3422, 0.17% in No. 3434, and <0.10% in all others.

The test samples divide into groups (Table II), with the rocks from districts 2 and 4 containing more carbonate than those from districts 3 and 5. The district 1 material is intermediate. The three test samples from each district, distinguished by original particle size of the rock, exhibit no within-district pattern.

Derived from Citrate and Citric Acid Solubility. Because the conventional determinations of available phosphorus by reaction of the rock with neutral ammonium citrate or citric acid involve timed reactions, they provide, by inference, a tentative classification of reactivity (6). The test ores again exhibit groupings when compared by mining region on this basis (Table III). Rocks from districts 1, 2, and 4 are generally more soluble in both neutral ammonium citrate and citric acid than those from districts 3 and 5, so that these independent measurements by and large place the rocks in the same order as the carbonate determinations above. There is no consistent relationship of solubility

to original particle size of the ore. The listing of three rocks from the general reactivity scale (6) at the foot of Table III shows that the differences between Florida rocks are small in comparison to differences between rocks from separate geographic areas.

Derived from Phosphoric Acid Reaction Rate. On the basis of the 10-minute index, the test Florida rocks fall into a comparatively narrow range of reactivity slightly below the Florida rock of the general scale, slightly above the Tennessee brown rock, and considerably below the Tunis rock (Table IV). Except for district 1, there is little difference between districts and no pattern with respect to original particle size of the ore. Two samples (lots 3423 and 3434) are apparently slightly more reactive than the others, reflecting features in their chemical constitution, such as low iron and aluminum content or high calcium-phosphorus ratios (Table II), that have been associated with high reactivity (9).

Reactivity and Physical Properties,

Table III. Solubility of 100- to 150-Mesh Fractions of Phosphate Rocks in Neutral Ammonium Citrate and 2% Citric Acid

Lot No. (Source)	% of Total P	
	Citrate-soluble	Citric acid-soluble
3422	8.6	20.4
3423	7.5	22.0
3424	8.6	19.7
Av.	8.2	20.7
3425	7.7	19.6
3426	6.0	17.6
3427	8.4	18.2
Av.	7.4	18.5
3428	7.8	20.0
3429	7.7	19.4
3430	6.6	18.1
Av.	7.4	19.2
3431	7.6	19.7
3432	8.7	20.2
3433	8.0	20.0
Av.	8.1	20.0
3434	8.2	20.2

Rocks from General Reactivity Scale^a

1551 (Tunis)	16.4	37.2
910 (Florida)	10.4	22.7
907 (Tennessee)	5.1	17.2

^a Data from Caro and Hill (3).

Table IV. Rate of Reaction of 100- to 150-Mesh Fractions of Phosphate Rocks in 30% H₃PO₄

Lot No. (Source)	10-Minute Rate Index	District Av.
3423	52.3	48.8
3424	45.0	
3425	46.2	
3426	41.5	44.4
3427	45.5	
3428	50.3	
3429	44.8	46.4
3430	44.0	
3431	44.7	
3432	46.5	45.1
3433	44.2	
3434	...	52.5

Rocks from General Reactivity Scale (6)

907 (Tennessee)	37.2
910 (Florida)	56.5
1551 (Tunis)	86.7

In view of the complexities of certain determinations, the measurement of physical properties was confined in the initial stages of the survey to one lot from each of the five mining districts. Results did not warrant extension of the measurements to the remaining samples. Properties measured included the surface area, true density, particle density, and porosity (Table V and Figure 2).

The surface areas vary rather widely, the range encompassing a considerable portion of the total range, from about 1 to

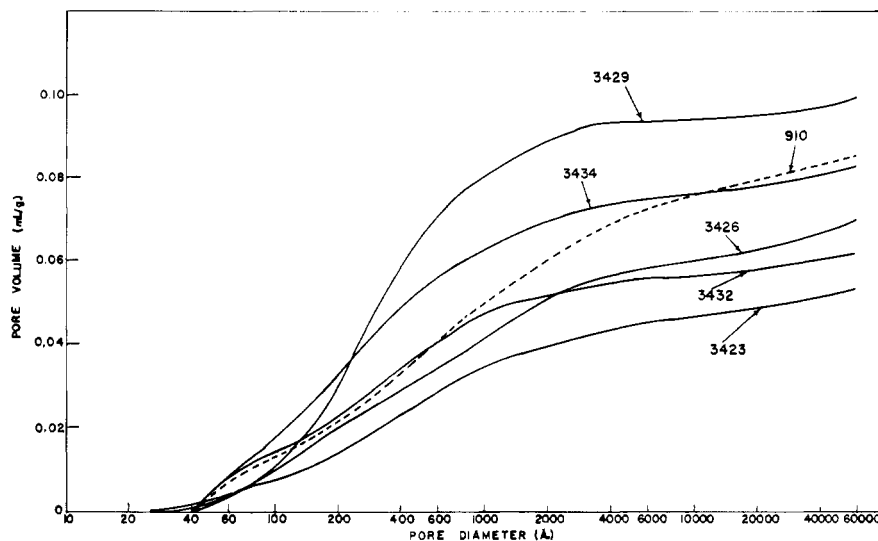


Figure 2. Porosity of Florida phosphate rocks

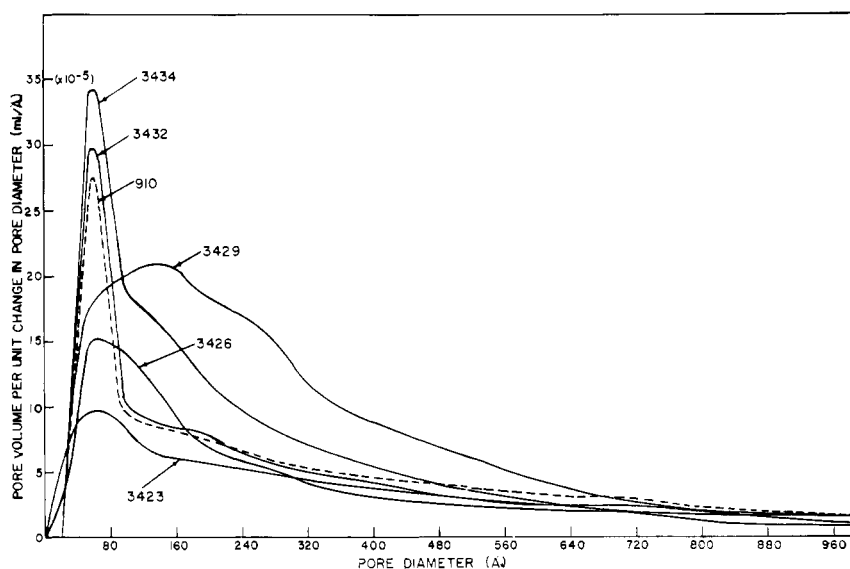


Figure 3. Pore size distributions in Florida phosphate rocks

about 30 square meters per gram, found in world-wide commercial deposits of phosphate rocks. However, total surface area does not necessarily have an important bearing on reactivity, because much of the surface in the interior of the particles may not be readily accessible to the reagent acid—for example, extent of surface area did not correlate with crop response in an earlier greenhouse test (3). Present results are in agreement with this—the rock of highest surface area is not outstandingly reactive, whereas the specimen with lowest surface area is one of the more reactive samples (Table IV).

True densities (Table V) show little variation, since all the rocks are of essentially the same gross constitution. The particle densities vary inversely with surface area, and the void volumes calculated from difference in densities increase directly with surface area. Physically, then, the district 3 rock (lot

3429) has the most open structure of those measured, while that from district 2 (lot 3423) is the least open. As with surface area, these structural variations are not sufficient to influence the reactivity as measured by reaction with phosphoric acid (Table IV).

That physical structure plays a less prominent role than chemical constitution in determining reactivity of these rocks is perhaps most clearly demonstrated by direct measurement of porosity (Figure 2), a property that has been studied comprehensively in a variety of phosphate rocks (2, 5). The pore volumes of the Florida rocks differ widely, almost to the same extent as do rocks from different geographic fields, yet bear no direct relationship to reactivity (Table IV). Probably a major reason for the insignificance of these variations in porosity is revealed in plots of the pore size distributions (Figure 3). While differences between Florida

Table V. Physical Properties of 100- to 150-Mesh Florida Phosphate Rocks

Lot No.	Surface Area, Sq. M./G.	True Density, G./Ml.	Particle Density, G./Ml.	Void Volume, ^a Ml./G.
3423	5.5	3.04	2.48	0.074
3426	6.7	3.03	2.41	0.084
3429	13.1	3.06	2.26	0.116
3432	9.3	2.97	2.37	0.085
3434	11.5	2.95	2.27	0.102

^a Calculated from:

$$\frac{1}{\text{particle density}} - \frac{1}{\text{true density}}$$

rocks are distinct, they are all well within one order of magnitude, whereas differences as large as three orders appear among rocks from separate geographic deposits (2).

"Typical" Florida Rock

It may be concluded that, while Florida rocks differ in both chemical and physical constitution, the differences are sufficiently small that a single selected specimen might more or less typify the entire deposit. It is of interest, then, to compare the properties of the Florida rock (lot 910) used as a component in the general scale of reactivity (6) with those of the rocks in the present study (Table VI) to ascertain its typicality. The comparison is especially interesting because rock 910 was an old specimen, mined in 1929. The intervening years have seen a marked advance in mining technology and changing economics of rock use, so that it might be questioned whether rock 910 still represents the Florida field.

Its chemical constitution differs from present-day products chiefly in iron content and in Ca/P ratio. The material was of inordinately high iron content even for its day (7), so that it has never been typical in that respect. On the other hand, the Ca/P ratio in Florida rocks has shown a general decrease through the years. Since this is one of the parameters cited as being conducive to high reactivity (9), rock 910 would be expected to be somewhat more reactive than the test rocks of the present study. This is confirmed by results for citrate and citric acid solubility and for the

Table VI. Properties of a 1929 Rock (Lot 910) Compared to Rocks from Recent Production (Lots 3422-3434)

Property	Units	Range, Lots 3422-3434	Lot 910
P content	%	12.7-15.2	13.5
Ca content	%	30.4-35.2	33.3
Ca/P	Wt. ratio	2.19-2.41	2.47
Fe ₂ O ₃ content	%	0.5-1.8	2.6 ^a
Al ₂ O ₃ content	%	0.7-2.2	1.1 ^a
F content	%	3.4-4.3	3.5
CO ₂ content	%	2.0-4.0	3.7
Citrate-sol. P	% of tot. P	6.0-8.7	10.4
Citric acid-sol. P	% of tot. P	17.6-22.0	22.7
10-minute rate index	...	41.5-52.5	56.6
Surface area	Sq. m./g.	5.5-13.1	9.9
Pore volume ^b	Ml./g.	0.054-0.099	0.085

^a Data from Jacob *et al.* (7).

^b Data abstracted from Figure 2.

10-minute rate index. Because the reactivities of rocks from other geographic deposits are so greatly different (Tables III and IV), that of rock 910 is close enough to the present Florida ores to be still considered representative.

In physical properties, rock 910 falls in all respects within the range of the present materials. The plot of pore size distribution (Figure 3) shows especially clearly that its structure remains typical of the field.

Conclusions

Small differences with respect to chemical constitution are noticeable between rocks from different locations within the Florida phosphate field. In general, the rocks divide into two groups. Those of relatively high carbonate content also have low contents of iron plus aluminum and high calcium-phosphorus ratios. This group is slightly more soluble in fertilizer solvents, but is only indistinctly more reactive in dilute phosphoric acid. Differences between Florida rocks and those from other deposits are much greater than the within-deposit variations, especially in the properties that are considered to influence relative reactivity.

Florida rocks vary widely in physical constitution, but no direct relationship of physical properties to relative reactivity could be found.

The 35-year-old rock used as the Florida representative in a previously established reactivity scale appears to be somewhat more reactive than material now being mined, but not sufficiently so as to be untypical of the deposit.

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