Characteristics and Fertilizer Value of Phosphate Rock from Different Fields

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As part of a systematic investigation of fertilizer value, solubility in fertilizer solvents, surface properties, physical properties of particles, and chemical composition of several types of phosphate rock were measured. Foreign rocks from Tunis and Curacao gave the highest solubilities, followed in order by domestic varieties from South Carolina, Florida, Idaho, Tennessee, and Virginia. The Tunis rock ranked highest and the Virginia apatite lowest in gas adsorption surface area and readily exchangeable phosphorus. Measurement of weight and density of closely sized particles indicated that the Tunis, Morocco, Florida, and South Carolina rocks were relatively light and of low density. Particle compactness lowers the reactivity of a rock. The chemical composition of the apatite component has appreciable influence on nutrient value. Statistical comparison of all laboratory measurements with crop yields in greenhouse culture showed that phosphate-bound carbonate content and citric acid solubility were the criteria giving best agreement.

THE USE OF GROUND PHOSPHATE ROCK for direct application to the soil has remained at a consistently high level in recent years, domestic consumption having exceeded 876,000 tons in 1953–54 (18). Rock for this use is supplied from three major domestic producing fields—Florida, Tennessee, and western United States. As these fields represent different geologic occurrences, rock mined from them exhibits differences not only in physical appearance but also in chemical composition (12) and in reactivity during processing (14).

Although difference in nutrient value would seem to be a logical expectation and was indeed demonstrated in greenhouse culture about a decade ago (5), little subsequent attention has been given this aspect of phosphate rock use. Recently, however, a systematic study was initiated in the branch, with a view to determining the fertilizer value of phosphate rocks from some important world producing fields when applied directly to the soil. Envisioned in this investigation were agronomic tests on materials that had been carefully characterized with the use of laboratory measurements of certain physical and chemical properties which might be presumed to influence vegetation response. The results of the laboratory measurements and their degree of correlation with the agronomic growth data are presented in this paper. The agronomic experiments are described elsewhere (2).

Test Materials

The chemical composition of the ten test rocks is given in Table I. The materials comprise rocks from three important foreign fields and seven domestic varieties. The domestic rocks include material from South Carolina which, though not being mined at present, showed a high nutrient value in previous tests (5), and Virginia apatite, which was selected on the suspicion that it would show a very low nutrient value, as well as materials from the three major producing fields.

The rock samples used in the investigation were prepared in the following manner: The lump rock was first crushed to −10 mesh. One portion of this −10-mesh material was then ground in a plate mill, adjusted to produce a grind containing about 50% of −100-mesh material. The ground sample was then parted by screening into −100+150-mesh, −150+325-mesh, and −325-mesh fractions. The other portion of the −10-mesh material was ground further to pass the 100-mesh sieve completely. The mechanical analyses of several of these −100-mesh composites are depicted graphically in Figure 1.

Table I. Chemical Composition of 100–150-Mesh Fractions of Phosphate Rocks

Lot No.	Variety or Source of Rock	P_2O_5, %	CaO, %	F, %	$CO_2{}^a$, %
1551	Tunis, Gafsa	29.9	44.3	3.6	5.8
2240	Morocco rock	32.1	51.6	4.2	5.5
1484	So. Carolina land rock	27.1	43.3	3.7	4.8
985	Curaçao Island	37.9	50.0	0.7	3.9
910	Florida land pebble[b]	30.9	46.6	3.5	3.7
1446	Florida land pebble[b]	33.2	44.7	3.5	2.0
1253	Idaho, Conda	33.0	47.1	3.4	1.8
907	Tennessee brown rock	35.0	48.6	3.7	1.3
1252	Montana, Garrison	36.4	50.5	3.9	1.3
1295	Virginia apatite	40.3	51.8	2.9	0.1

[a] CO_2 found as free calcite by method of Silverman, Fuyat, and Weiser (19): 1551, 0.3; 2240, 0.6; 1484, 0.2; 985, 0.6; 910, 0.0; 1446, 0.0%.
[b] Flotation concentrate.

Experimental Procedures

Citrate Solubility. The solubility in neutral ammonium citrate solution was determined by the official procedure of the Association of Official Agricultural Chemists (3), except that ammonium nitrate was not added to combat cloudiness of filtrates. The method involves agitation of 1 gram of sample in 100 ml. of citrate solution for 1 hour at 65° C. with subsequent determination of phosphorus in the insoluble residue.

Citric Acid Solubility. Determination of the solubility in 2% citric acid solution, formerly an official AOAC procedure for available phosphorus in basic slag (4) and still an official method in most foreign countries (11), was carried out at both 17.5° C. (official) and 24° C. Two grams of sample were agitated for 30 minutes in 200 ml. of the acid and filtered, and dissolved phosphorus in the solution was determined.

Surface Area. Specific surface areas were determined by means of the Brunauer-Emmett-Teller (BET) nitrogen adsorption technique (6), which depends upon the adsorption of a monolayer of nitrogen near the boiling point of liquid nitrogen. Measurements were made in the Bone Char Research Project at the National Bureau of Standards.

Readily Exchangeable Phosphorus. A technique for estimation of surface area, employed earlier with dicalcium phosphate (7), was applied to the test rocks. In this method, an aqueous phosphate solution containing radioactive phosphorus-32 is allowed to come in contact with the sample and the mixture is agitated. The surface phosphorus (phosphorus-31) which exchanges with the radioactive isotope in solution is determined by periodic measurement of solution radioactivity and an assay of solution phosphorus concentration at the conclusion of the reaction. Experimental quantities used with phosphate rock were 1 gram of sample and 100 ml. of a tagged solution of monopotassium phosphate having an initial concentration of about 10 γ of phosphorus per ml.

Weight and Density. Particle weight and density were measured on the 100-150-mesh fractions of the test rocks. Average particle weights were obtained by count under a reading glass of 10 groups of 50 particles each, followed by weight determination of each group on a microbalance. Densities were found by displacement of glycerol in a small buret by 5-gram portions of the rocks. Glycerol was employed because its high surface tension and viscosity minimize liquid penetration into the pores of the phosphate particles.

Characteristics of Test Materials

Solubility in Fertilizer Solvents. The results for citrate and citric acid solu-

bilities of the test rocks are given in Tables II and III, respectively. Both measurements place the materials in substantially the same order of solubility. The foreign rocks from Tunis and Curaçao clearly outrank all domestic varieties, except that the South Carolina rock is on a par with the Curaçao sample in the neutral citrate test. Of the domestic varieties, the South Carolina and Florida rocks gave a considerably higher result than those from Idaho and Tennessee. The Virginia apatite, which produced a very poor vegetative response in the greenhouse study (2), is also shown to rank low in the solubility tests, especially with citric acid.

The influence of particle size on solubility follows a regular pattern within the screened fractions. A small but consistent increase in soluble phosphorus with decrease in particle dimension is exhibited. The solubility of the −100-mesh composites, on the other hand, does not fall into the pattern, in several cases indeed showing a higher result than that given by the corresponding −325-mesh fraction. This circumstance may be the result of the additional grinding operation to which these preparations were subjected.

The influence of digestion temperature on the result for citric acid–soluble phosphorus is illustrated by figures determined at 17.5° (specified in the procedure formerly used by AOAC) and at 24° C. (Table III). The results at the latter temperature, though higher, are consistently so, and do not change
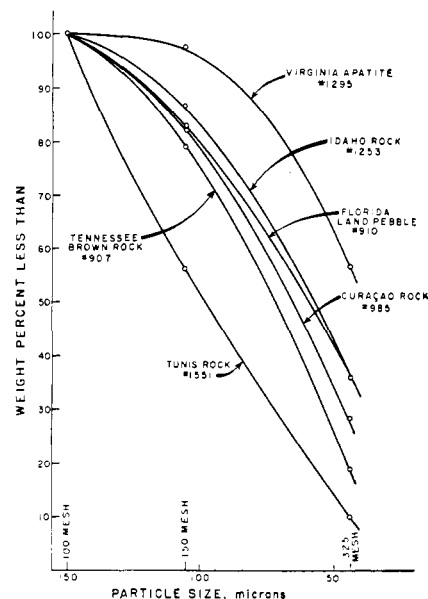

Figure 1.   Mechanical analyses of −100-mesh phosphate rocks

the order of the materials with respect to solubility.

Surface properties. The gas-adsorption surface areas of the test rocks (Table IV) show highest surfaces for the Tunis, Florida, and Tennessee varieties. There is only an ill-defined relationship with particle size. These observations, which contrast markedly with the solubility pattern discussed above, may be ascribed to the physical inhomogeneity of the

Table II.   Solubility of Sized Portions of Phosphate Rocks in Neutral Ammonium Citrate

		Citrate-Soluble P_2O_5, % of Total			
Lot No.	Variety or Source of Rock	−100-mesh composite	100-150-mesh fraction	150-325-mesh fraction	−325-mesh fraction
1551	Tunis, Gafsa	20.0	16.4	16.5	18.9
1484	So. Carolina land rock	17.2	10.0	14.7	15.7
985	Curaçao Island	14.8	11.9	12.0	14.6
910	Florida land pebble	11.1	10.4	10.5	14.4
1253	Idaho, Conda	7.8	4.5	7.8	10.6
1295	Virginia apatite	7.6	1.5	5.8	6.4
907	Tennessee brown rock	6.1	5.1	5.1	7.1

Table III.   Solubility of Sized Portions of Phosphate Rocks in 2% Citric Acid

		Citric Acid-Soluble P_2O_5, % of Total							
		−100-Mesh Composite		100-150-Mesh Fraction		150-325-Mesh Fraction		−325-Mesh Fraction	
Lot No.	Variety or Source of Rock	At 17.5° C.	At 24° C.	At 17.5° C.	At 24° C.	At 17.5° C.	At 24° C.	At 17.5° C.	At 24° C.
1551	Tunis, Gafsa	35.4	37.8	34.4	37.2	37.8	40.3	43.7	45.7
985	Curaçao Island	36.4	38.8	32.3	33.8	35.2	37.4	39.0	40.6
1484	So. Carolina land rock	24.6	27.0	21.8	24.2	23.6	25.7	23.9	26.4
910	Florida land pebble	22.3	24.1	20.7	22.7	22.3	23.9	23.6	24.7
1253	Idaho, Conda	19.8	21.8	17.4	19.5	20.3	23.1	26.5	28.4
907	Tennessee brown rock	16.4	18.6	15.0	17.2	16.2	18.5	17.5	19.1
1295	Virginia apatite	10.3	11.5	3.3	4.9	4.8	6.6	7.1	8.6

Table IV. Surface Area of Sized Portions of Phosphate Rocks

Lot No.	Variety or Source of Rock	Specific Surface, Sq. M./G.			
		—100-mesh composite	100–150-mesh fraction	150–325-mesh fraction	—325-mesh fraction
1551	Tunis, Gafsa	15.6	19.4	19.1	22.5
910	Florida land pebble	9.3	10.3	7.5	12.5
907	Tennessee brown rock	7.8	6.8	6.4	8.7
985	Curaçao Island	5.5	3.6	3.7	7.8
1484	So. Carolina land rock	4.7	6.5	3.9	5.8
1253	Idaho, Conda	4.4	3.0	3.3	6.0
1295	Virginia apatite	1.1	0.6	0.7	1.5

Table V. Readily Exchangeable Phosphorus of Sized Portions of Phosphate Rocks

Lot No.	Variety or Source of Rock	Readily Exchangeable Phosphorus, γ/G.			
		—100-mesh composite	100–150-mesh fraction	150–325-mesh fraction	—325-mesh fraction
1551	Tunis, Gafsa	510	425	430	a
985	Curaçao Island	785	215	340	620
910	Florida land pebble	245	195	265	510
1484	So. Carolina land rock	505	95	145	235
907	Tennessee brown rock	225	130	165	335
1253	Idaho, Conda	265	105	150	200
1295	Virginia apatite	195	12	70	105

a Result by routine determination inaccurate, owing to high sorptivity of sample.

Table VI. Physical Characteristics of 100–150-Mesh Phosphate Particles

Lot No.	Variety or Source of Rock	Av. Particle Weight, γ	Av. Apparent Particle Density, G./Cc.	Equivalent Sphere Diameter, μ
1551	Tunis, Gafsa	2.6	2.71	122
910	Florida land pebble	2.8	2.78	124
2240	Morocco rock	3.0	2.66	129
1446	Florida land pebble	3.0	2.74	128
1484	So. Carolina land rock	3.1	2.70	130
985	Curaçao Island	3.2	2.86	129
907	Tennessee brown rock	3.4	2.83	132
1252	Montana, Garrison	3.8	3.13	132
1253	Idaho, Conda	4.0	2.89	138
1295	Virginia apatite	4.2	3.15	137

material. Phosphate rock is composed of aggregates of very small grains that are several orders of magnitude smaller than the aggregate dimension (10). As these constituent grains are not agglomerated in a uniform manner (9), any physical property, such as surface area, that involves consideration of the internal structure of the aggregates, is subject to considerable variation.

Seemingly more important as a criterion of agronomic value is that part of the gas-adsorption surface which is subjected to the leaching action of soil water under growth conditions and which is presumed to control the rate of reaction of the rock in the soil. The extent of this "accessible surface" is closely identified with that of the contact surface between sample and solution in isotope exchange measurements of surface phosphorus (7). Results for readily exchangeable phosphorus (a measure of the contact surface) in the test rocks are given in Table V. The ranking of individual varieties displays a considerable degree of similarity to that pre-sented by the solubility in neutral citrate or citric acid (Tables II and III).

Physical Characteristics of Rock Particles. The weight and apparent density of average particles of the 100–150-mesh fractions of the test rocks are given in Table VI along with the equivalent sphere diameter. The latter is the diameter of a sphere having the weight and density shown, and is thus an expression of the mean particle volume. It reflects the net result of diverse size and shape of the particles. For 100–150-mesh material, a set of perfect spheres uniformly distributed throughout the sieve range would give an equivalent diameter equal to the mean of the sieve openings, 127 microns. Since eight of the ten rocks listed in the table display equivalent sphere diameters within 5 microns of this mean, effective cancellation of shape and size variation among particles is suggested. The particle weight and density listed are thus essentially equivalent magnitudes.

When tabulated in order of ascending particle weight, the rocks fall into the general order of suitability found by other laboratory measurements. As the size of the particles is the same, both particle weight and density reflect the degree of compactness of the material. The extent of surface is also markedly influenced by the compactness, or lack of pore space. There is thus a close relationship between the listed properties and the surface area of the material. It appears that physical compactness, as denoted by high particle weight or density or low surface area, lowers the reactivity of a rock.

Composition of Apatite Component. That the chemical composition of apatite, the principal phosphorus-bearing component of a phosphate rock, should influence its reactivity both in the soil and in chemical processing is to be expected. Information on the relationship between composition and reactivity has been sought for many years. Of special interest in this connection are the fluorine and carbonate contents (Tables I and VII).

The role of fluorine is not very clear. This element is generally regarded as the principal agent by which phosphate is rendered insoluble and stored in nature. A plausible extension of this idea is that the presence of fluorine makes the phosphate less reactive. Indeed, low-fluorine rock, such as that from Curaçao Island, is more soluble in citrate solution, for example, than are some rocks that carry larger complements of this element (Tables I and II). Nevertheless, other rocks that carry fluorine in excess of that required by the fluorapatite formula (8) are even more soluble than Curaçao phosphate.

Table VII. Degree of Carbonation and Fluorination of Phosphate Rocks

Lot No.	Variety or Source of Rock	$CO_2:P_2O_5$ Wt. Ratio	$F:P_2O_5$ Wt. Ratio
1551	Tunis, Gafsa	0.194	0.120
1484	So. Carolina land rock	0.177	0.137
2240	Morocco rock	0.171	0.131
910	Florida land pebble	0.120	0.113
985	Curaçao Island	0.103	0.018
1446	Florida land pebble	0.060	0.105
1253	Idaho, Conda	0.055	0.103
907	Tennessee brown rock	0.037	0.106
1252	Montana, Garrison	0.036	0.107
1295	Virginia apatite	0.002	0.072

The relatively large percentage of carbon dioxide contained in soluble, highly fluorinated rocks emphasizes the importance of this constituent. These rocks exhibit, in addition to the high solubility, very small grain size, which is accompanied by a correspondingly high surface area and low particle density. The presence of moderate amounts of carbon dioxide (other than in the form of calcite) has long been regarded as desirable in rock used for superphosphate manufacture. Such rock reacts better and yields a product with the coveted crumbliness. Furthermore, the highly carbonated rock from North Africa is said to be more efficacious as a soil additament than is rock that carries less carbon dioxide (16, 17).

The presence of phosphate-bound carbon dioxide possesses a special significance with regard to apatite structure. When the test rocks were treated by a method described by Silverman, Fuyat, and Weiser (19) for determination of the distribution of carbon dioxide among mineral constituents of apatites, the results showed that almost all the carbonate was apatite bound rather than present as free calcite (Table I, footnote[b]). With use of x-ray diffraction techniques, evidence for the presence of lattice-bound carbonate has been presented by Altschuler, Cisney, and Barlow (1) for phosphate rock and by Trautz and coworkers (20) for bone and tooth enamel. The apatite constituent of phosphate rock, in general, appears to be hydroxyl-fluorocarbonate-apatite, in which hydroxyl is replaced more or less completely by fluorine and the phosphate group is partially replaced by carbonate ions (13). The occurrence of fluorapatite, as well as nearly fluorine-free hydroxylapatite and hydroxyl-carbonate-apatite in nature (15), is evidence that the two indicated substitutions may be mutually independent, the extent of each being limited by both environmental conditions and structural considerations. In any event, the degrees of fluorination and of carbonation are salient chemical properties of the apatite class of phosphates. Fluorination lowers the reactivity, whereas carbonation enhances it, and the influence of the latter process often more than compensates for the effect of the former.

Laboratory Tests as Criteria of Agronomic Quality

Inasmuch as the foregoing properties of the phosphates were chosen for measurement on the presumption that they are instrumental in regulation of crop response, their usefulness as indexes of fertilizer value should be reflected by agreement between the laboratory tests and crop yields in greenhouse culture. The closeness of agreement is shown with the use of correlation coefficients in

Table VIII. Correlation of Laboratory Measurements with Yield of Alfalfa[a] on Acid Soils Fertilized with 100–150-Mesh Phosphate Rocks

	Correlation Coefficients		
Relationship, Yield vs.	Crosby silt loam	Elliott sandy loam	Cecil sandy loam
Bound CO_2 content[b,c]	0.88[d]	0.90[d]	0.88[d]
Citric acid–soluble P_2O_5[e]	0.96[d]	0.92[f]	0.93[d]
Citrate-soluble P_2O_5[e]	0.86[g]	0.88[f]	0.87[f]
Particle density[c]	0.79[f]	0.83[f]	0.76[g]
Particle weight[c]	0.72[g]	0.78[f]	0.74[g]
Readily exchangeable P[e]	0.76	0.67	0.81
Surface area[e]	0.56	0.56	0.70

[a] As reported by Armiger and Fried (2).
[b] Table I, total CO_2 less calcite CO_2.
[c] Based on ten observations.
[d] Significant at 0.1% level.
[e] Based on seven observations.
[f] Significant at 1% level.
[g] Significant at 2% level.

Table VIII. Comparison on this basis of the respective measured properties results in a division into three distinct groupings:

1. Good.   Bound carbonate content
               Citric acid solubility

2. Intermediate.   Citrate solubility
                   Particle density
                   Particle weight

3. Poor.   Exchangeable phosphorus
             Surface area

The citrate solubility, which is in universal use in this country as a measure of phosphorus availability, is somewhat inferior to the carbonate content and the citric acid solubility when applied to these rocks. The very high correlation obtained with the carbonate content introduces a new index into present-day fertilizer technology. However, it is necessary to distinguish the bound carbonate from the free calcite. Should a rock be tested which contains large amounts of calcite (not the case with the sample rocks of this study), measurement of total carbon dioxide content alone could lead to highly erroneous interpretations.

Acknowledgment

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