

ethyl alcohol. The trihydrate was prepared by addition of the anhydrous salt to a melt of the tetrahydrate until the liquid was saturated at 50° C. The supernatant liquid was decanted off, cooled to 45° C., and seeded, whereupon the mass solidified as the trihydrate. The tetrahydrate was crystallized from its solution in water through use of published data on the system  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$  (7).

#### Properties of the Compounds

The morphological and optical properties of the hydrates of calcium nitrate, summarized in Table II, were observed on several preparations of each hydrate; these properties are sufficient for identification, even when the hydrate is still in its mother liquor. The bipyramidal form of the dihydrate is a useful distinguishing feature, and the birefringence of the dihydrate is more than double that of the trihydrate. Both the tri- and the tetrahydrate usually form highly

modified, thick, tabular crystals that are not readily distinguished morphologically, but the extreme birefringence of the tetrahydrate, its low  $N_x$  (below that of the mother liquor), and its monoclinic symmetry serve to distinguish it from the trihydrate. Anhydrous calcium nitrate is cubic and has a refractive index of 1.602.

The x-ray powder diffraction pattern of the di- and trihydrates of calcium nitrate are shown in Table III. Patterns of the anhydride and tetrahydrate agree with those in the ASTM card index (7-204 and 1-0229).

The crystal morphology of calcium nitrate tetrahydrate in Table II agrees with that reported by Marignac (5, 6). The optical properties determined in a laboratory preparation and ascribed by Larsen (3) to the tetrahydrate agree with those reported here for the trihydrate. The trihydrate is orthorhombic, not triclinic as reported by Bassett and Taylor (7). The dimorphic form

of the tetrahydrate described by Flatt and Fritz (2) was prepared, but its dry crystals altered so rapidly to the stable tetrahydrate that it could not be characterized.

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## FERTILIZER MATERIALS

### Effect of Calcination on the Character of Phosphate Rock

Two varieties of phosphate rock were calcined under conditions of controlled temperatures and retention times. Physical and chemical properties were measured on the laboratory calcines and on five commercially calcined rocks. Results showed that the response to calcination differs with rock variety. With increasing temperature, a Morocco rock exhibited a sharp collapse of the internal structure of the particles between 500° and 700° C., whereas a Utah rock was less affected. Solubility of phosphorus decreased in the Morocco rock but increased to a maximum at 850° C. in the Utah rock. Changes occurring in both rocks with increase in retention time were pronounced but slow, so that close control of heating time was not necessary. Reactivity of both rocks was decreased by calcination, but the decrease was frequently insignificant. The commercially calcined rocks were apparently treated under conditions corresponding to the threshold of the structural collapse, so that maximum benefits of calcination are being routinely realized.

**A**N APPRECIABLE proportion of the phosphate rock mined throughout the world is heated in some sort of furnace before being introduced into fertilizer or animal feed. The objectives of this treatment fall into two broad categories, distinguishable by the temperatures used. In general, processes conducted above 1000° to 1100° C. remove the fluorine and, with use of additives, allow chemical reactions to occur that make the phosphate in the rock available (76). Treatments below

1000° C. are carried out to increase the grade of the mineral, remove objectionable organic matter and carbonate, and improve acidulation characteristics, with accompanying economic advantages. Other effects include improvement in grindability and decrease in bulk density (73).

The higher temperature treatments bring about gross changes, such as sintering or fusion, that are readily apparent on examination of individual particles of the rock. The changes oc-

curing at the lower temperatures, on the other hand, are not well defined. This paper reports the results of a systematic examination of the character of rocks from different geographic deposits as affected by low-temperature calcination.

#### Scope of Investigation

The study was designed to allow description of the changes in phosphate rock effected by variation in both

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temperature and time of heating. For comparison, specimens of commercially calcined rocks were included along with those prepared in the laboratory. Characterizations, carried out on both calcined and uncalcined test samples, consisted of measurement of surface area, pore volume, pore size distribution, true density, particle density, relative reactivity, weight loss, and contents of total  $\text{CO}_2$ , bound  $\text{CO}_2$ , total and citrate-insoluble phosphorus, and fluorine.

### Materials and Methods

Phosphate rocks from the Morocco, Utah, Florida, and Peruvian fields were used. Samples representative of material fed to the calciner as well as of the calcined products were obtained from commercial sources and screened, by wet sieving, to 100 to 150 mesh for characterization. Portions of the screened fractions of the Morocco and Utah calciner feed materials were also subjected to controlled calcinations in the laboratory, the two varieties being chosen because earlier work had shown them to be of recognizably different reactivities. North African deposits are, typically, very reactive, whereas the rocks in the western U. S. fields exhibit only moderate reactivity (7). The test rocks were generally representative of their respective fields, except that the Utah material contained little if any dolomite (Figure 7), reported to be the dominant carbonate mineral in Western phosphate rocks (6, 15).

To ascertain the effect of temperature, two series of test samples were prepared by heating separate 15- to 20-gram portions of the Morocco rock for  $1\frac{1}{2}$  hours in a laboratory muffle furnace, one portion at  $450^\circ\text{C}$ . and succeeding portions at each  $100^\circ$  increment up to  $1150^\circ\text{C}$ ., and repeating the entire series with the Utah rock. To ascertain the effect of retention time, one series of samples was similarly prepared by heating 15- to 20-gram portions of the Morocco rock at  $650^\circ\text{C}$ . for times ranging from 30 minutes to 2 weeks. The heated specimens from all three series were then characterized along with the commercial calcines.

Surface areas were determined by nitrogen adsorption measurements at  $78^\circ\text{K}$ ., using the BET method (3). Pore volumes and size distributions were obtained by a combination of nitrogen desorption at  $78^\circ\text{K}$ . and mercury porosimetry (4).

The term "total pore volume" refers to the volume of all pores finer than 40,000 A. in diameter, which is the upper limit of accurate measurement with the techniques and particle sizes employed; "fine pore volume" refers to the volume contained in pores of 0- to 600-A. diameter, which is the size range influencing rock reactivity (4). Although the minimum measurable pore size is limited by the size of the nitrogen molecule (about 4 A.), it is considered to be effectively zero.

True density, which refers to the compact solid material of which the rock

is composed, was determined by displacement of helium (10). Particle density, which refers to solid material plus interior voids, was measured by displacement of mercury. A simple densitometer (Figure 1) was designed to allow rapid measurement of particle density. In operation, the volume of the evacuated sample tube, both empty and containing a weighed sample, is measured by filling with mercury from the buret. Density is calculated from the difference in the two volumes.

The relative reactivity of a rock was estimated by measuring its rate of reaction with dilute phosphoric acid. A 1-

gram portion of rock reacted with 5 ml. of 30%  $\text{H}_3\text{PO}_4$  for 10 minutes. The reacted mixture was rapidly filtered, the residue copiously washed with water, and the citrate-insoluble phosphorus content determined. The citrate-soluble phosphorus expressed as a percentile of the total phosphorus content constitutes the reactivity index.

Apatite-bound carbonate, known to be an excellent indicator of crop response to direct application of a rock (5), was determined by routine analysis of the residue after dissolution of the free carbonate (calcite) in a solution of triammonium citrate (14).

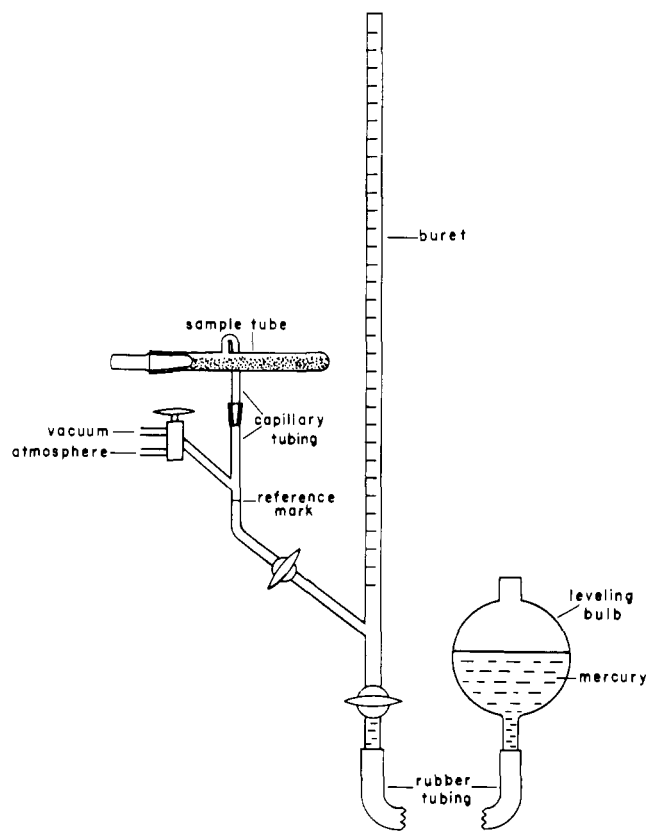


Figure 1. Mercury densitometer

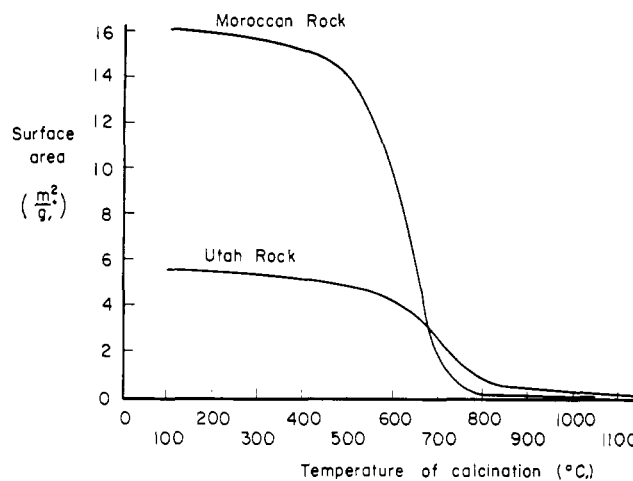


Figure 2. Effect of calcination temperature on surface area of two varieties of laboratory-calcined phosphate rock

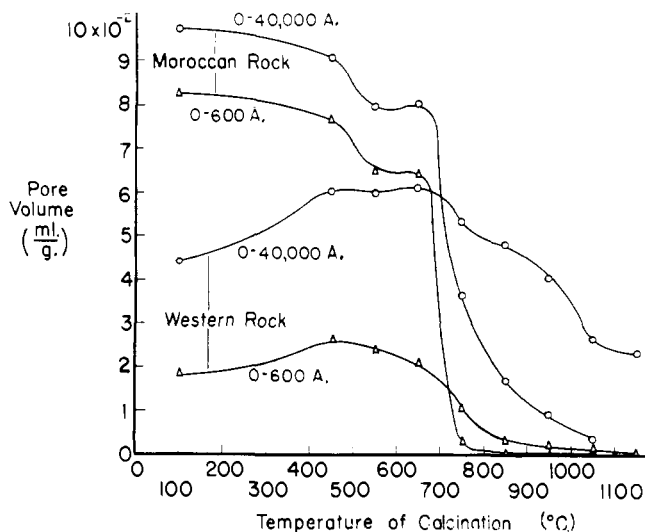


Figure 3. Effect of calcination temperature on total and fine pore volume in two varieties of laboratory-calcined phosphate rock

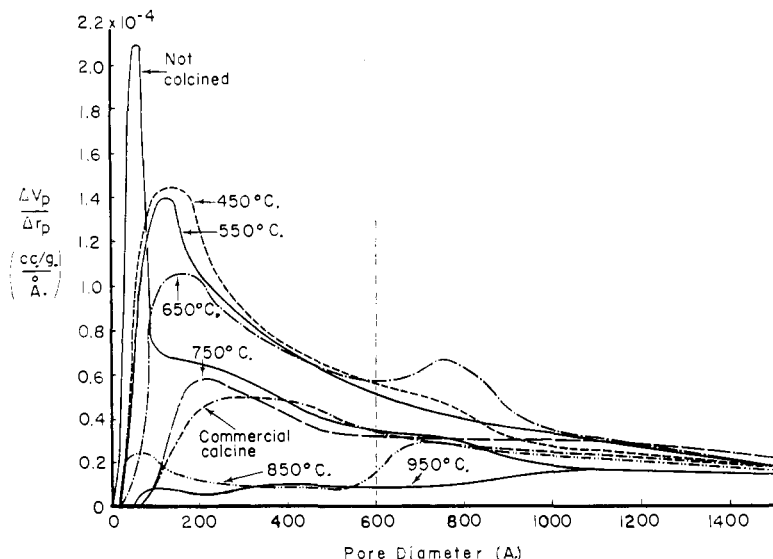


Figure 4. Effect of calcination temperature on pore size distribution in Utah rock

### Physical Structure of Calcined Rocks as Influenced by Temperature of Calcination

**Surface Area.** The surface area of calcined phosphate rock decreases with increasing temperature of calcination, as shown in Figure 2. The most striking feature of the curves is the sharp break, especially pronounced in the Morocco rock, in the 500° to 700° C. region. Since particles of phosphate rock are composed of aggregates of elementary grains roughly 50 to 300  $\mu$  in size (8), the break suggests that consolidation of these very small grains occurs at these temperatures. As a matter of fact, particle fusion occurred in both rocks during laboratory calcination. It was more prevalent and began at a lower temperature (650° to 750° C.) in the Morocco rock than in the Utah rock (850° to 950° C.). The change in structure may be more clearly visualized

in the examination of pore size distribution, described below.

A second point of interest in Figure 2 is the transposition of the two rocks at about 700° C. On calcination above 700° C., the Utah rock has a higher surface area than the Morocco variety, so that, on physical grounds at least, it may be presumed to be the more reactive rock. This observation has a bearing on the later discussion of relative reactivity.

**Porosity and Pore Size Distribution.** The porosity of the two rocks in the temperature series is shown in Figure 3. Since the upper of each pair of curves shows the total pore volume and the lower the fine pore volume, the vertical distance between each pair obviously represents the volume of coarse pores, 600 to 40,000 A. in diameter. It is immediately apparent that the observed changes occur principally in the fine pores. Only at temperatures above

800° C. does a decrease in coarse porosity become evident in both rocks. Reference to Figure 2 reveals that these coarse pores contribute negligible surface area to the material.

In the main, the porosity of both rocks changes in a manner similar to the surface area. The general trend is downward, the sharp breaks occur, and the two rocks transpose at 700° C. However, there are two noteworthy differences. The first is the increase in porosity that occurs when Utah rock is calcined at temperatures below 500° C., an effect observed previously with Israel rock (7). The rise, which involves both coarse and fine pores, actually takes place while the surface area shows a gradual decrease (Figure 2). This apparent anomaly can best be explained on the basis of the volatilization of organic matter, which occurs in appreciable quantities in Western rock. Removal of this matter from pore walls and particle interstices could increase the porosity while decreasing the surface area. Pore size distribution within each broad size class (coarse and fine) would be shifted in the direction of coarser pores, and this too has been observed (Figure 4).

The second point of distinction between the porosity and surface area curves of both rocks is the hump that occurs between 550° and 650° C., a range in which the surface area is decreasing sharply. This effect is distinct from the lower temperature anomaly discussed above. The mechanism is revealed in the complete pore size distributions (Figures 4 and 5). Between 550° and 650° C., there is a decided shift among the fine pores in the direction of coarseness. The probable cause is collapse of thin internal walls within the particles prior to the general structural collapse between 650° and 750° C.

The pore size distribution curves (Figures 4 and 5), which are plots of the relative pore volume at each pore size, show further, and more clearly than does Figure 3, that temperature-induced changes in porosity occur primarily in the fine pore region. The sharp drop in the pore volume of the Morocco rock between 650° and 750° C. is again demonstrated (Figure 5), as is the lesser decrease for the Utah rock calcined at the same temperatures (Figure 4). Curves for commercially calcined samples of each rock, discussed later, are included on these plots to allow direct comparison.

**Density.** The true densities of both rocks in the temperature series (Table I) were somewhat lower than the reported values, 3.16 to 3.22, for fluorapatite (2). The difference may be ascribed to the presence of nonapatitic components and, presumably, to the unavailability of some internal spaces to the helium used in the measurement. Both rocks show

little change in true density on calcination below 750° C. Above that temperature, erratic changes occur. Perhaps fortuitously, a plot of these changes in Utah rock almost parallels the curve of relative reactivity (Figure 6). The very sharp drop in true density occurring on calcination of Utah rock at 1150° C. (Table I) suggests the occurrence of a crystal transition at this temperature.

Changes in particle density (Table I) generally reflect the internal collapse of the particles at 650° to 750° C., with transposition of the two rocks again occurring at about 700° C. The particle density thus constitutes a simply measured property that gives a rough comparative measure of internal physical structure.

### Effect of Calcination Temperature on Chemical Composition

**Phosphorus.** The grade of calcined rock rises with temperature of calcination (Table I). The increase is associated with the volatilization of non-phosphatic constituents such as hydrocarbons, water of crystallization, and inorganic carbonates. No loss of phosphorus is evident even at the highest temperatures employed, since calculation on the basis of weight loss (last column) gives a phosphorus level at least equal to that of the uncalcined material.

The citrate-soluble phosphorus content, a measure of reactive phosphorus, shows a generally decreasing trend with increasing temperature of calcination of the Morocco rock, whereas with Utah rock, an increase to a pronounced peak at 850° C. is evident. This unexpected behavior is interpreted below in the discussion of relative reactivity.

**Carbonate.** Considerable heat is required to effect substantial removal of carbonate from phosphate rock. Even after calcination at 750° C. for 1½ hours, over one third of the carbonate remains in Morocco rock, and the volatilization from Utah rock is similar (Table I). The scattered measurements seem to indicate that apatite-carbonate and calcite-carbonate (difference between total and apatite-carbonate) are volatilized at the same rate in the Morocco rock, whereas calcite-carbonate is more easily given off in the Utah rock.

**Fluorine.** Little fluorine was volatilized from the test rocks at the temperatures used in this study.

### Effect of Calcination Temperature on Rock Reactivity

The reactivity of a phosphate rock is an inherent property of the mineral that influences its rate of reaction with acids (7). While it is widely held that calcination results in a decrease in reactivity (13), the work reported here supports the view that rocks from different geographic deposits respond differently

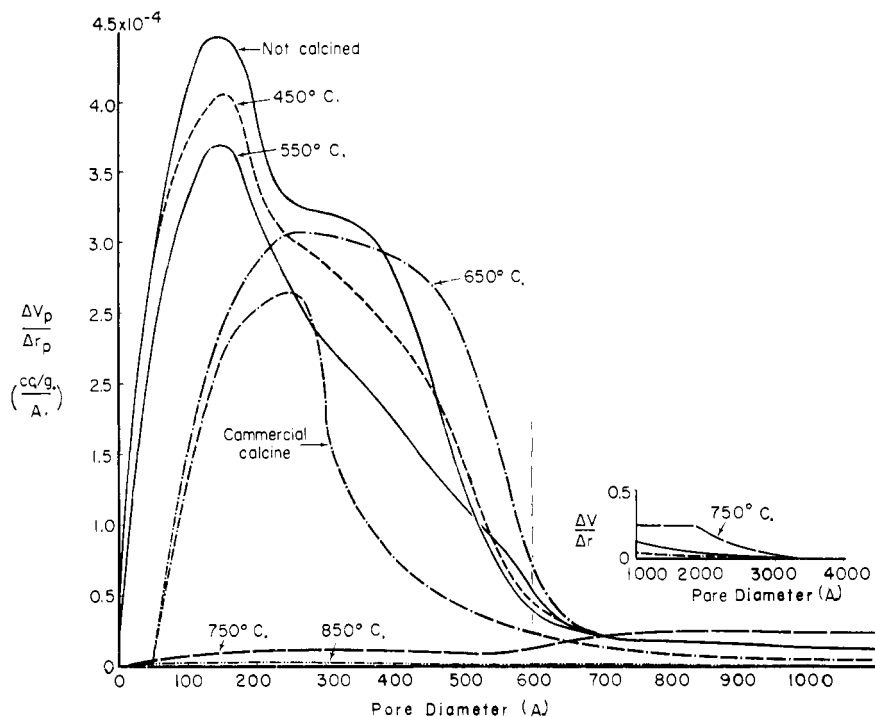


Figure 5. Effect of calcination temperature on pore size distribution in Morocco rock

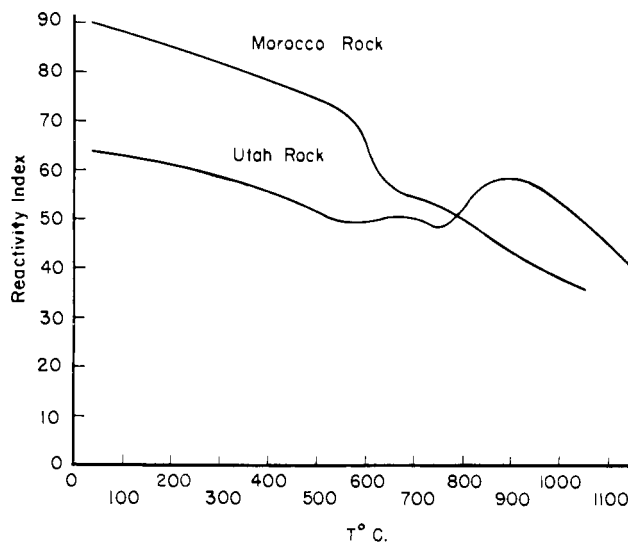


Figure 6. Effect of calcination temperature on relative reactivity of Morocco and Utah phosphate rocks

to calcination and that the decrease is sometimes negligible.

Thus, the relative reactivity of the two test rocks in the temperature series is shown in Figure 6. Although the reactivity does decrease in both rocks, there is an important difference in the behavior of the two varieties. The drop in reactivity of the Morocco rock with increasing temperature is pronounced and uninterrupted, with a sharp decrease at 600° to 700° C. corresponding to the structural collapse. In Utah rock, on the other hand, the decrease is less definite and an actual increase, peaking at 850° to 900° C.,

occurs at the higher temperatures. Clearly, the source of the rock is a key consideration with respect to heat-induced changes in reactivity.

The physical structure of a rock undoubtedly is the major factor controlling its reactivity, as witnessed by the shape of the curves and the transposition of the two test rocks in the independently measured plots of relative reactivity, surface area, and porosity. However, evidence points to a chemical transition as the cause of the high-temperature peak in the reactivity of Utah rock. Thus, both the citrate solubility of the phosphorus and the true density show

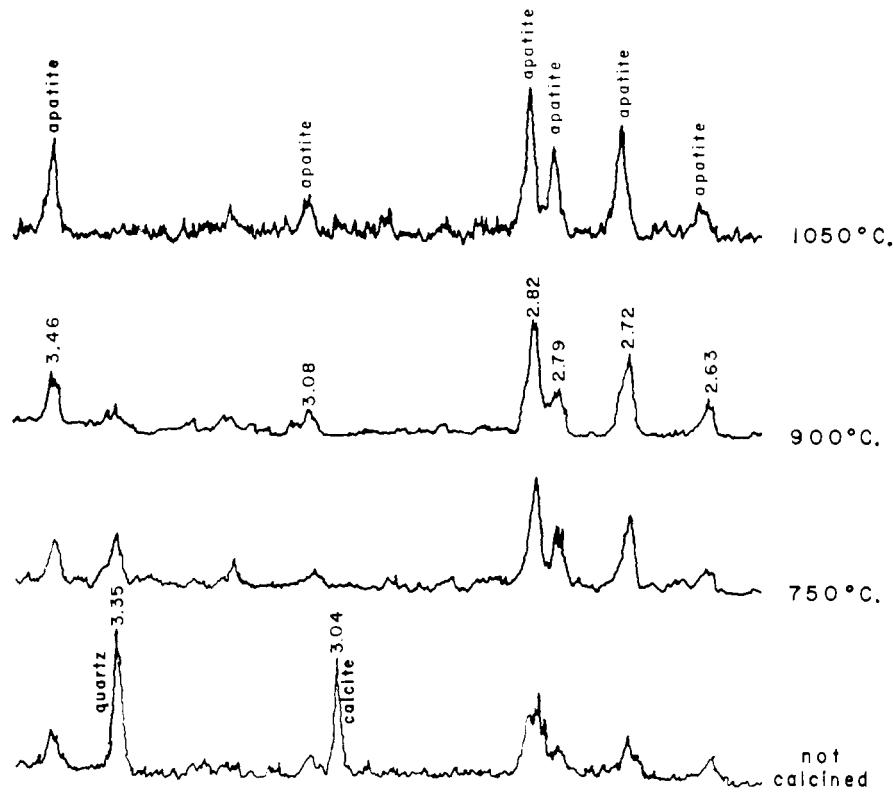


Figure 7. X-ray diffraction patterns of Utah rock calcined at different temperatures

Table I. Properties of Morocco and Utah Phosphate Rocks Calcined at Different Temperatures for 1 1/2 Hours

Calcination Temp., ° C.	Content					True Density, G./Ml.	Particle Density, G./Ml.	Weight Loss, %
	Total P (P <sub>2</sub> O <sub>5</sub> ), %	Cit.-sol. P or P <sub>2</sub> O <sub>5</sub> , % of tot.	Total CO <sub>2</sub> , %	Apatite-CO <sub>2</sub> , %	Fluorine, %			
MOROCCO ROCK (SWC 3515a)								
Not calcined	14.0 (32.0)	17.0	5.2	4.8	4.6	3.07	2.26	...
450	14.7 (33.6)	11.9	...	...	...	3.05	2.28	2.1
550	14.7 (33.6)	9.4	4.9	4.5	4.1	3.03	2.25	2.3
650	14.9 (34.2)	6.8	...	...	4.4	3.02	2.24	3.5
750	15.5 (35.4)	8.6	1.9	1.4	...	3.03	2.65	5.8
850	15.5 (35.6)	6.7	...	...	...	2.96	2.80	6.4
950	15.6 (35.8)	3.4	0.8	0.6	4.3	3.06	2.83	6.9
1050	15.4 (35.3)	1.8	...	...	...	3.07	2.89	7.9
UTAH ROCK (SWC 3509)								
Not calcined	13.0 (29.8)	3.2	2.7	1.6	3.7	3.01	2.54	...
450	13.5 (30.9)	2.5	2.6	1.8	3.5	3.03	2.48	3.2
550	13.7 (31.4)	4.2	2.3	1.6	...	3.01	2.48	4.3
650	13.8 (31.5)	5.7	...	...	...	3.01	2.46	4.9
750	14.1 (32.2)	7.0	...	...	3.3	2.96	2.52	5.6
850	14.2 (32.5)	14.7	0.5	0.5	3.4	3.08	2.74	5.8
950	14.1 (32.4)	8.9	...	...	...	3.09	...	7.5
1050	14.6 (33.4)	8.1	...	...	...	3.03	2.68	8.2
1150	14.5 (33.2)	1.9	0.0	0.0	3.2	2.74	...	8.5

Table II. Properties of Morocco Phosphate Rock (SWC 3515a) Calcined at 650° C. for Different Periods of Time

Retention Time, Hr.	Content					True Density, G./Ml.	Particle Density, G./Ml.	Weight Loss, %
	Total P (P <sub>2</sub> O <sub>5</sub> ), %	Cit.-sol. P or P <sub>2</sub> O <sub>5</sub> , % of tot.	Total CO <sub>2</sub> , %	Apatite-CO <sub>2</sub> , %	Fluorine, %			
Not calcined	14.0 (32.0)	17.0	5.2	4.8	4.6	3.07	2.26	...
0.5	15.2 (34.7)	9.6	...	...	...	3.00	2.26	2.6
1	15.1 (34.5)	7.6	3.7	3.4	...	2.99	2.29	3.2
2	15.4 (35.3)	8.4	...	...	3.9	3.02	2.39	3.5
3	15.5 (35.4)	8.3	...	...	...	3.03	2.39	4.0
6	15.5 (35.5)	7.2	2.9	2.3	...	3.05	2.37	4.3
16	15.6 (35.8)	6.8	...	...	4.3	3.04	2.50	5.3
48	15.8 (36.1)	7.1	1.7	1.2	...	3.09	2.46	5.5
1 week	15.8 (36.3)	7.3	...	...	...	3.10	2.45	5.6
2 weeks	16.0 (36.6)	...	...	...	...	...	...	6.0

**Table III. Properties of Commercially Calcined Phosphate Rocks**

SWC Lot No.	Source of Rock	Treatment	Content					True Density, G./Mi.	Particle Density, G./Mi.
			Total P (P <sub>2</sub> O <sub>5</sub> ), %	Cit.-sol. P or P <sub>2</sub> O <sub>5</sub> , % of tot.	Total CO <sub>2</sub> , %	Apatite-CO <sub>2</sub> , %	Fluorine, %		
3521	Florida	Not calcined	15.6 (35.7)	7.5	2.4	2.2	4.3	3.10	2.38
3513	Florida	Calcined, 815° C.	16.2 (37.0)	5.8	2.0	2.0	4.1	3.01	2.36
3522	Florida	Not calcined	14.8 (33.8)	7.8	2.9	2.8	3.8	3.10	2.40
3514	Florida	Calcined, 815° C.	15.5 (35.5)	6.4	2.2	2.2	3.2	2.97	2.46
3509	Utah	Not calcined	13.0 (29.8)	3.2	2.7	1.6	3.7	3.01	2.54
3501	Utah	Calcined, 775° C.	14.4 (33.0)	9.1	1.2	0.8	3.7	3.02	2.57
3515a	Morocco	Not calcined	14.0 (32.0)	17.1	5.2	4.8	4.6	3.07	2.26
3515b	Morocco	Calcined, 910° C.	16.6 (38.0)	6.0	0.7	0.5	4.3	3.22	2.72
3496	Peru	Not calcined	13.7 (31.3)	18.0	4.6	4.2	3.6	3.00	2.34
3497	Peru	Calcined, 900° C.	14.9 (34.2)	9.9	0.1	0.1	3.7	3.03	2.67

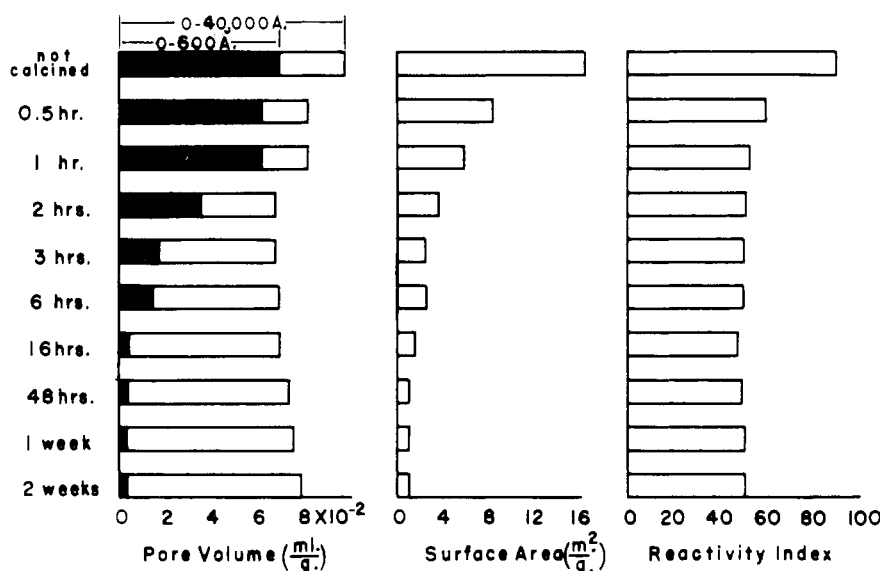


Figure 8. Effect of retention time on properties of Morocco rock calcined at 650° C.

similar peaks (Table I). Nunez (12) has found increasing activity of silica in Florida rock calcined in the same temperature range; and excessive formation of sludge, presumably resulting from heightened activity of iron and aluminum in the rock, has occurred in wet-process phosphoric acid made from calcined Utah rock. In an effort to identify the transition, x-ray diffraction patterns were obtained for those specimens calcined at pertinent temperatures (Figure 7). The three effects to be noted from these patterns are: the disappearance of quartz in the range 750° to 1050° C., the disappearance of calcite below 750° C., and the sharpening of the apatite lines with increasing temperature. No new crystalline phase appears at high temperatures, suggesting the development of glass structures. The transition sought might involve the slow conversion of quartz to silicocarnotite (9), but further research is obviously needed for confirmation.

**Character of Calcined Phosphate Rock as Influenced by Retention Time**

Morocco rock calcined at 650° C. was selected for study of retention time because at this point in the temperature series the structure of the material began to collapse (Figure 3). The changes in properties with time of calcination are shown in Figure 8 and Table II.

**Physical Properties.** The surface area (Figure 8) decreases regularly with retention time until, at 48 hours' heating, it approximates that of the same rock heated at 750° C., the next highest temperature in the temperature series (Figure 2). The total pore volume, on the other hand, shows only a slight decrease to a minimum at 2 hours' heating, then increases slowly but steadily. Pore size distribution shifts markedly in the direction of coarse pores. Thus, after extended heating at 650° C., a low-surface, coarsely porous material is obtained that is physically analogous

to the product of short-term heating at about 725° C. (Figures 2 and 3).

After an initial decrease, the true density (Table II) shows a slight increase on prolonged calcination. The drop may be caused by occlusion of very fine pores in the material and the subsequent rise may be the result of slow volatilization of a low-density component. The continuing weight loss through two weeks' calcination is evidence of the latter. The particle density also shows a continuing increase, which is undoubtedly associated with the broadening of the pores to allow deeper penetration of the mercury into the particles.

**Chemical Properties.** As in the temperature series, the grade of the rock rises as volatile matter is evolved with time (Table II). The heat-induced reduction in citrate-soluble phosphorus content, noted earlier, is here shown to be rapid. Little subsequent change in phosphorus solubility occurs with increase in retention time. Changes in

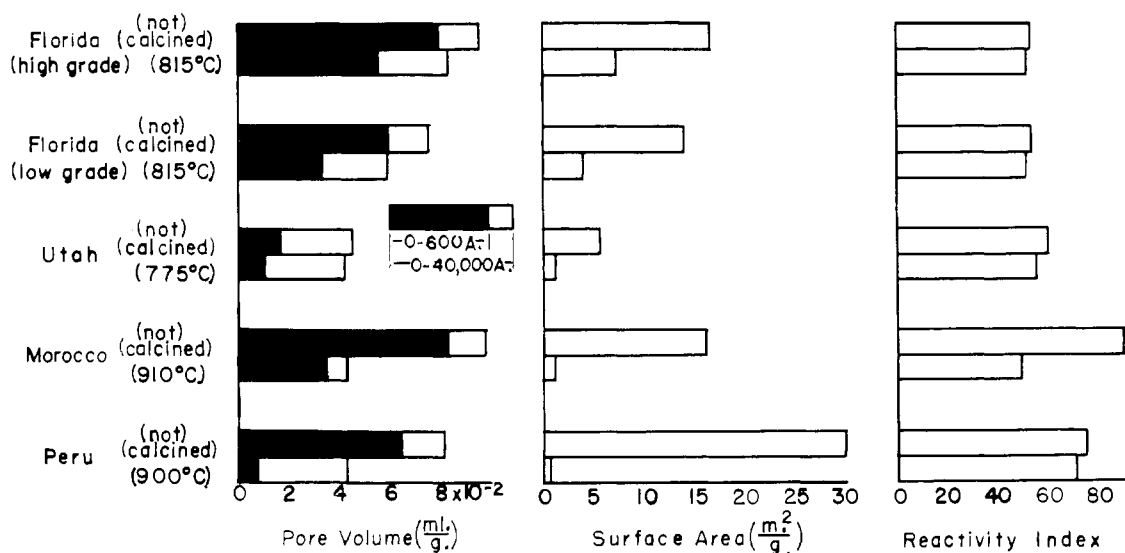


Figure 9. Physical properties and relative reactivity of commercially calcined phosphate rocks

relative reactivity (Figure 8) parallel those in phosphorus solubility. Carbonate is evolved slowly at this temperature, and fluorine is almost completely retained.

#### Character of Commercially Calcined Phosphate Rocks

The treatment given rock calcined by commercial processors differs appreciably from that to which experimental batches are subjected in the laboratory. Commercial processes involve large beds of material moving through a high-temperature zone in a large-capacity roasting chamber while being tumbled or fluidized by forced drafts. Laboratory calcination, on the other hand, consists of the quiescent roasting of small batches by uniformly applied heat in a muffle furnace. It is of interest, then, to compare the properties of several commercial products and to relate them to those of the experimental calcines discussed above. Accordingly, the properties of five commercial products are shown in Figure 9 and Table III, in direct comparison with the respective calcine feed materials.

**Physical Properties.** Changes produced in physical structure seem to be sensitive to the temperature of the commercial process, as might well be expected from our previous observations. Thus, the pore volume (Figure 9) is only slightly reduced in the three varieties of rock calcined at less than 900° C., whereas a much sharper change occurs in the other two rocks. A similar effect may be noted with respect to surface area (Figure 9) and particle density (Table III). However, in every case the decrease in porosity occurs almost entirely in the fine pores.

The detailed pore distribution of the commercially calcined Utah and Morocco rocks (Figures 4 and 5, respectively) shows that both materials were treated under conditions corresponding to the threshold of the structural collapse. In light of the sharpness of the break in the latter rock, it is apparent that careful study has gone into process design to optimize the benefits to be gained from calcination. Just a slightly higher temperature or somewhat lengthened retention time would yield a product having much less desirable physical characteristics. Since these materials were obtained more or less at random from industrial sources, one may infer that optimum conditions are routinely achieved in commercial calcination practice.

Since most of the surface area is contained in the fine pores, the decrease in surface naturally parallels that in fine pore volume (Figure 9). A vivid illustration of the dependence of surface area on extent of fine pores is provided by the Peruvian rock. This material, which exhibited an extreme drop in surface area on calcination, contains in its natural state 73% of its pore volume in pores of less than 200-A. diameter. None of the other rocks shown has more than 42% of its pores in this range.

The true density of the rocks is little affected by commercial calcination except in the case of the Morocco variety (Table III). The increase in density of this material is probably associated with its leaching with ammonium chloride subsequent to calcination to remove excess lime; hence, it is not actually a result of the calcination.

**Chemical Properties.** The increase in grade brought about by calcination is less in Florida rocks than in those

from other fields (Table III). A contributing factor is the stronger retention of carbonate in Florida varieties, an effect that had also been observed in earlier studies. Since Florida rocks contain little or no calcite (5), all the carbonate is presumably bound into the apatite lattice and is more difficult to remove.

The citrate-soluble phosphorus content of the commercial calcines (Table III) provides an ample illustration of the differences between rock varieties with respect to the effect of calcination on phosphorus reactivity. The content is sharply decreased in the Morocco and Peruvian rocks, moderately decreased in the Florida rocks, and sharply increased in the Utah rock. A similar increase has been reported for Christmas Island rock (11). The data for the temperature series (Table I) show that the increase in the Utah variety could be made still greater by a small further increase in temperature.

Relative reactivity as given by the reactivity index (Figure 9), which reflects rate of solubilization of phosphorus rather than amount solubilized, shows only that little change occurs on calcination except in the case of the Morocco rock. One may infer from this that the progressive decrease in reactivity in this variety with increasing temperature (Figure 6) is not characteristic of most rocks.

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## PROPERTIES OF FERTILIZER MATERIALS

### Metal Potassium Phosphates

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Because very little information is available on the properties of the metal potassium phosphates, data are presented on their composition, K ( $K_2O$ ) and P ( $P_2O_5$ ) availabilities, solubilities, thermal stabilities, and x-ray diffraction spectra. The solubilities of  $MgKPO_4 \cdot H_2O$  and  $MgKPO_4 \cdot 6H_2O$  in water, dilute HCl, and NaOH are slightly higher than the corresponding magnesium ammonium phosphates. Magnesium potassium phosphate dissolves incongruently. X-ray diffraction data indicate that the monohydrate, upon digestion in water at room temperature, is completely converted to the hexahydrate over a period of about 100 hours and that  $Mg_3(PO_4)_2 \cdot 22H_2O$  is present in the residue. Thermogravimetric analyses indicate complete dehydration of magnesium potassium phosphate monohydrate at  $150^\circ$  to  $160^\circ$  C. and of the hexahydrate at  $60^\circ$  to  $70^\circ$  C.

THE METAL potassium phosphates are a series of compounds having the general formula  $MeKPO_4 \cdot xH_2O$ , where Me is a divalent metal ion and  $x$  is 0, 1, or 6. Metals which form compounds of this type are magnesium, manganese, copper, zinc, cobalt, nickel, and cadmium (2).

The metal potassium phosphates are only slightly soluble in water. As with metal ammonium phosphates (3), this property suggested their use in non-burning and long-lasting fertilizers. A mixture of metal ammonium phosphates and metal potassium phosphates could supply essentially all the necessary plant nutrients in a nearly water-insoluble form.

Magnesium potassium phosphate is a very efficient source of both potash and phosphate (5). Good response was reported with tomatoes, ryegrass, and other crops. Response depended on granule

size making it possible to tailor potassium and phosphorus supply for a given crop or cropping period. The soluble salt level in soils was reduced by using  $MgKPO_4 \cdot H_2O$  rather than the usual potash sources. The compounds seemed well suited to supply nutrients close to the plant in direct seeded crops (5).

The other metal potassium phosphates are potential sources of trace elements. These materials can be mixed with other fertilizers to supply the necessary trace elements. The quantities added would depend on factors such as crop requirements and soil deficiencies; however, the trace element usage would probably not exceed more than about 1 to 2% of the fertilizer.

The compounds are similar both chemically and physically to the metal ammonium phosphates (3). This is to be expected because the ammonium ion and potassium ion are approximately the same size—i.e., 1.42 Å. and 1.33 Å., respectively. There are many examples of isomorphism between ammonium and potassium compounds.

The metal potassium phosphates could be used as a research tool by agronomists to study the interactions of K and P with various trace metals in much the same way as metal ammonium phosphates can be used to study N-P-metal interactions. All of the compounds are similar chemically except for the variation in the metal in combination with either ammonia or potassium. Having several plant nutrients together in a single compound might be different agronomically than mixtures of compounds containing the same nutrients.

The rate of release of nutrients from magnesium ammonium phosphate and magnesium potassium phosphate is different from particles of the same size. This is probably due to the fact that the rate of release of nitrogen from magnesium ammonium phosphate is affected by nitrifying bacteria, whereas the potassium salt does not have this type of breakdown. Presumably the nutrients are released from magnesium potassium phosphate only by solubility. Therefore, the rates of release of nutrients

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