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PLANT NUTRIENT VALUE OF FERTILISERS BASED ON CALCIUM PHOSPHATES,

by

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I N D E X

	Page
1. <u>INTRODUCTION</u>	1
1.1. Phosphate fixation in the soil.....	1
2. <u>REACTIONS OF CALCIUM PHOSPHATES WITH WATER</u>	2
3. <u>MATERIALS</u>	3
3.1. Monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$	3
3.2. Dicalcium phosphate dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	3
3.3. Dicalcium phosphate, CaHPO_4	3
3.4. Hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	3
4. <u>REPEATED AQUEOUS EXTRACTION OF CALCIUM PHOSPHATES</u> ...	4
4.1. Results and Discussion.....	4
4.1.1. Monocalcium phosphate.....	5
4.1.2. Dicalcium phosphate dihydrate.....	6
4.1.3. Dicalcium phosphate, anhydrous.....	7
4.1.4. Hydroxyapatite.....	8
5. <u>SCALE OF RELATIVE FERTILISER VALUES</u>	8
5.1. Comparison with plant growth tests.....	10
5.2. Evaluation of mixtures of calcium phosphates, such as are found in fertilisers.....	11
5.3. Possible improvements in the method.....	11
6. <u>SUMMARY AND CONCLUSIONS</u>	12
7. <u>REFERENCES</u>	13

PLANT NUTRIENT VALUE OF FERTILISERS BASED
ON CALCIUM PHOSPHATES

INTRODUCTION

This paper discusses one approach to the problem of assessing the relative plant nutrient values of some phosphates commonly found in fertilisers. A primary aim of the work in which the study originated was to examine possible differences in value between the phosphates rendered water-insoluble during the manufacture of ammoniated mixed fertilisers based on superphosphate and the water-soluble phosphate in non-ammoniated fertilisers of otherwise similar composition. It was accepted at the start that this problem hinges on differences in the behaviour of the various calcium phosphates when introduced into soil, since the effect of ammoniation is to increase the basicity of the calcium phosphates present.

applied to the soil

In our view phosphate can only be transferred from fertiliser to plant through the medium of the soil solution. If the phosphate concentration of the solution in contact with a fertiliser is too low to permit optimum rate of absorption by the plant, then the fertiliser cannot be an efficient form of phosphate for immediate application. We have, therefore, based our conclusions on the results of repeated aqueous extractions of different calcium phosphates, together with published data on their decomposition in the presence of water. Plant nutrient values of these phosphates cannot be reliably and conveniently assessed from a consideration of the results of (a) conventional tests of solubility in water or other solvents, or of (b) plant growth experiments in the field or greenhouse.

Conventional solubility tests, depending upon which one is chosen, tend to show a phosphate fertiliser as being more or less available to the plant than is really the case. For example, the water solubility test, ascribes little or no value to dicalcium phosphate dihydrate. On the other hand, citric and citrate solubility tests regard virtually all its phosphate content as being available. It is our view that on most soils neither answer is the correct one. Whilst the growing plant must be the eventual arbiter of phosphate availability, it is understandable that the fertiliser manufacturer developing a new product does not wish to have that development slowed down to the pace set by plant growth tests. This is especially true in the early stages of development. Field tests of a new product should be spread over at least two or three years, and a very large amount of effort is required since the treatments must be highly replicated if a precision of only 10% is to be obtained. Variable factors such as the weather, the types of soil, the types of crop and different lengths of growing season, etc., all contribute to the difficulty of making assessments from field trials and pot tests.

It is well known that the absorption of phosphate by a plant is affected to a considerable extent by soil-fertiliser reactions. We shall now examine these reactions in a qualitative way in order to predict how the properties of the fertiliser are likely to affect phosphate uptake. This is a necessary preliminary to a discussion of the relative potential values of phosphate fertiliser. It will be useful at this stage to explain our terminology; "relative" is used because (as will be described later) we have taken two substances to represent high and low points on our scale of availability, and the term "potential" is used because we refer to the maximum fertilising value that a material is capable of supplying in one growing season and discount the effects of different types of soil on phosphate fixation.

1.1.

Phosphate fixation in the soil.

When a soil in equilibrium with its soil solution is treated with a fertiliser phosphate, the equilibrium will be disturbed. Phosphate ions will be dissolved from the added solid, and simultaneously (but not necessarily at the same rate) similar ions will be removed from solution by adsorption reactions occurring at the surfaces of soil colloids and also by precipitation reactions. The/

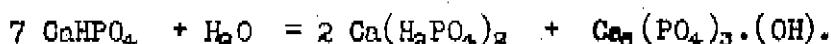
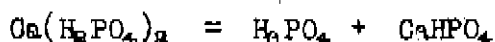
The phosphate concentration in the soil solution at any one time will, therefore, be determined by a number of considerations, two important ones being the solubility and rate of solution of the added phosphate and the phosphate adsorbing properties of the soil. When a state of equilibrium has been attained in the system soil/soil solution/phosphate-source, subsequent removal of phosphate from solution by the plant will be followed by solution of phosphate from one or other of the solid phases in an attempt to maintain equilibrium. If replenishment of the dissolved phosphate occurs at the same speed as the plant requires it, then the plant will receive sufficient phosphate for its needs. On the other hand, if replenishment proceeds more slowly than this, then the plant will suffer from phosphate deficiency. If we assume that the soil solution is the sole source of phosphate for growing plants, it is clear that the dissolved phosphate must be replaced many times during the growing season. Stout and Overstreet (1950) have shown that the rate of such replacement must be several times daily.

It follows from this much simplified picture of phosphate behaviour in soil that two important factors controlling the potential availability of a phosphate fertiliser are (1) rate of solubility in the soil solution, and (2) the fraction of its phosphate content which will eventually dissolve to give a concentration high enough to maintain an adequate supply of phosphate to the plant in the face of absorption by the soil colloid surfaces. A study of the properties of mono- and dicalcium phosphates and of hydroxyapatite, with particular reference to these factors, has provided a basis for the assessment of the relative potential values of these materials.

2.

REACTIONS OF CALCIUM PHOSPHATES WITH WATER.

The partial disproportionation of calcium phosphates when treated with water has been well known for some time (e.g. Warrington, 1873; Joly, 1883). Monocalcium and dicalcium phosphates react as follows:



It is probable that the value of a fertiliser based on calcium phosphate, as measured in the year of application, is limited by the amount of disproportionation which occurs, since one of the products of decomposition is slower to dissolve than the material originally present. As a result it is less likely to make available the whole of its phosphate in a reasonable time after application, i.e. during the growing season.

Sanfourche & Focet (1933) studied the decomposition of hydrated monocalcium phosphate in contact with water. They showed that the amount of disproportionation occurring in 2 hours increased with increasing salt:water ratio. In their most dilute solutions (less than 1.3 g. monocalcium phosphate/100 g. water) they found that disproportionation did not occur. At 20°C., the amount of M.C.P. decomposed was 40.7% of the total M.C.P. present; this was in a system in which solid $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was in contact with its saturated solution (70 g. of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 100 \text{ g. water}$).

However, Elmore and Farr (1940) have calculated that the maximum decomposition of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ that can occur in aqueous systems at 35°C. is 56.5%, this being in a system containing 48.5% monocalcium phosphate, 51.5% water. The discrepancy between the two sets of results is presumably due to differences in experimental conditions. Sanfourche and Focet worked at a temperature 5° lower than that used by Elmore and Farr; they allowed less time for the system to attain equilibrium (2 hours compared with 10 months), and their most concentrated system was more dilute than that which Elmore and Farr reported as corresponding to maximum decomposition.

The disproportionation of dicalcium phosphate in presence of water has been studied by Sanfourche and Henry (1933). They equilibrated amounts of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ varying from 0.1-10 g. with 1 litre volumes of water for 10 days/

days at about 20°C. and found that disproportionation only occurred when a few mg. of tricalcium phosphate were added to the suspension and that the extent of such disproportionation depended upon the weight of dicalcium phosphate used. At 0.1 g./litre no decomposition was detected. The amount of monocalcium phosphate formed increased to a maximum (equivalent to 58% of the total P_2O_5 in solution) with 1 g. solid present and then decreased with increasing amounts of solid, falling to 33% of the total dissolved P_2O_5 in the system to which 10 g. $CaHPO_4 \cdot 2H_2O$ /litre had been added.

We have obtained additional information on the decomposition of some calcium phosphates by determining the amount of phosphate brought into solution by successive aqueous extractions, and this work is described below.

3.

MATERIALS.

3.1.

Monocalcium phosphate, $Ca(H_2PO_4)_2$.

Prepared by recrystallisation from 80-90% phosphoric acid solution at 125°C., Hill & Hendricks (1936).

3.2.

Dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$.

Prepared by reaction of phosphoric acid and a suspension of calcium hydroxide at a temperature below 30°C.

3.3.

Dicalcium phosphate, $CaHPO_4$.

Prepared by suspending the dihydrate in 3% aqueous phosphoric acid at 70°C. for 24 hours. The product, which was slightly basic as compared with the theoretical composition, was washed with dry acetone and dried at 50°C.

3.4.

Hydroxyapatite, $Ca_5(PO_4)_3(OH)$.

The term "hydroxyapatite" is here used to describe a precipitated basic calcium phosphate with molar ratio, $CaO/P_2O_5 = 3.33$, corresponding to the formula $Ca_5(PO_4)_3(OH)$. It is possible to obtain precipitated calcium phosphates of widely differing compositions all of which give apatite-like X-ray diffraction patterns (Eisenberger et al., 1940). It is also possible for precipitates of composition $CaO/P_2O_5 = 3.33$ to consist of mixtures owing to insufficient time having been allowed for equilibration at the time of making.

Our material was prepared by adding the calculated amount of lime in a slurry to dilute phosphoric acid at 95°C. over a period of 4 hours. At the end of this time the pH of the suspension was 7.2. The precipitated solid was dried at 95°C. for 48 hours. The CaO/P_2O_5 ratio of the product was close to the theoretical value, and it is believed that the method of preparation was likely to give a homogeneous product. X-ray examination did not show the presence of any contaminant, and confirmed that the material was substantially hydroxyapatite.

Analyses of these materials are given in Table I which also shows the theoretical compositions. The hydroxyapatite contained water which was not lost on heating for 24 hours at 110°C. and this explains the low P_2O_5 and CaO contents.

TABLE I. /

TABLE I.

Analyses of calcium phosphates

(Theoretical values in brackets).

	P ₂ O ₅ %	CaO %	CaO/P ₂ O ₅ molar
Monocalcium phosphate	60.8 (60.65)	23.9 (23.96)	1.00 (1.00)
Dicalcium phosphate dihydrate	41.3 (41.24)	32.9 (32.59)	2.02 (2.00)
Dicalcium phosphate	51.0 (52.17)	41.1 (41.21)	2.04 (2.00)
Hydroxyapatite *	39.3 (42.39)	52.8 (55.82)	3.40 (3.33)

* Loss on ignition at 850-900°C. = 5.96%

REPEATED AQUEOUS EXTRACTION OF CALCIUM PHOSPHATES

Extractions of the four reference calcium phosphates were each carried out at 2 ratios of solid/water. In the case of the lower ratio the amount of phosphate was fixed at a weight likely to be substantially dissolved in 18-20 extractions each with 100 ml. of water; the higher ratio was 10 times the lower. It is not practicable to do this with monocalcium phosphate, which is extremely soluble in water. In this case the quantities of solid and water used for the lower ratio extraction were chosen to be comparable with those used in the United Kingdom official water-soluble P₂O₅ determination. The higher ratio was again 10 times the lower.

The method of extraction was as follows. The solid phosphate was weighed into a centrifuge bottle and 105 ml. water was added (25 ml. in the case of monocalcium phosphate). The bottle and contents were mechanically shaken for 30 min. and then centrifuged; the supernatant liquid subsequently being removed for analysis. A further volume of water was added to the solid residue, and shaking and centrifuging were repeated. Phosphate was determined in each extract and also in the residue remaining after the series of extractions. When sufficient residue remained its calcium content was also determined. No intervals were allowed between the extractions in a series, and the cycle of operations was carried out with as much regularity as possible. In this way the amount of disproportionation occurring in the period between removal of solution and addition of a fresh volume of water was kept to a steady minimum. Each sample of monocalcium phosphate was extracted twice only, since the residues were then of composition similar to that of dicalcium phosphate. The dicalcium phosphates were both extracted 18 times, and the hydroxyapatites 12 times. The concentration of carbon dioxide in the water used was maintained below 0.01 millimolar. The work was carried out at a temperature of 20°C. ±2°.

Results and discussion

Figure 1 shows the phosphate concentrations of the extracts of the two dicalcium phosphates and of hydroxyapatite. Similar data for monocalcium phosphate are given in Table 2.

TABLE 2./

TABLE 2.

Phosphate concentrations of extracts of monocalcium phosphate

Extract No.	P ₂ O ₅ , g./litre	
	Low solid/water ratio	High solid/water ratio
1	14.3	122
2	0.26	7.6

The amounts of P₂O₅ left undissolved after the extractions are given in Table 3 which also shows the solid/water ratios used in the first extraction. The final column gives values of the molar ratio CaO/P₂O₅ for some of the residues.

TABLE 3.

Analyses of residues after extractions

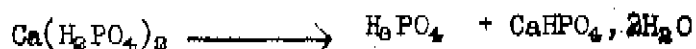
Material	Ratio solid/water in 1st extraction g./l.	P ₂ O ₅ in residue as % of original P ₂ O ₅	CaO/P ₂ O ₅ molar
Monocalcium phosphate	24.9	4.0	n.d. ^R
"	249	14.5	1.96
Dicalcium phosphate dihydrate	0.57	0.3	n.d.
"	5.81	53	2.27
Dicalcium phosphate	0.49	14	n.d.
"	4.90	85	2.06
Hydroxyapatite	0.15	39	n.d.
"	1.53	89	3.26

^R

n.d. = not determined.

4.1.1. Monocalcium phosphate. The residue from the higher solid/water extractions was shown by X-ray to be a mixture of CaHPO₄·2H₂O and CaHPO₄, the former predominating. Hydroxyapatite would not have been detected by this technique if less than 10% were present. Determination of CaO/P₂O₅ ratio confirmed that the residue was substantially dicalcium phosphate. In the low solid/water experiment, the amount of residue was too small to permit an accurate calcium determination, but it is probable that this residue also consisted of dicalcium phosphate.

The point of most interest is the comparison between the decomposition of anhydrous monocalcium phosphate and that of the hydrate, as reported by Sanfourche & Focet (1933). If we assume that decomposition occurs as in the equation:-



then the amount of monocalcium phosphate which has decomposed can be calculated from the amount of residual dicalcium phosphate. Thus, from the results of Table 3 we have that the amounts of decomposed monocalcium phosphate were not less than 8% and 29% of the total monocalcium phosphate in the low and high solid/water extractions respectively. Sanfourche and Focet found 6.7% and 32.3% respectively for comparable solid/water ratios, when using the hydrated phosphate. These two sets of/

of results are in fair agreement, and we conclude that there is little, if any difference between the hydrated and anhydrous salts as regards their decomposition with water under conditions of this kind.

As mentioned above, the best figure that has been given for the maximum decomposition of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is probably that of Elmore and Farr (1940), and we therefore assume that their value (56.5%) applies to the anhydrous salt also.

When this salt is applied to the soil as a fertiliser, the limited amount of soil solution in contact with it can be expected to induce the maximum decomposition*. We may conclude then that the net potential fertilising effect of monocalcium phosphate is equivalent to adding 72% of its P_2O_5 in a "stable" soluble form (e.g. as ammonium phosphate) and the remaining 28% as dicalcium phosphate (i.e. $\frac{1}{2}$ of Elmore and Farr's value of 56% decomposition).

4.1.2.

Dicalcium phosphate dihydrate. In the low solid/water ratio experiment this salt gave a concentration of about 0.06 g. P_2O_5 /litre in each of the first three extractions; 88% of the total P_2O_5 had then been dissolved. Subsequent extracts showed much lower concentrations (see Figure 1) and after thirteen extractions no further phosphate could be dissolved. It is likely that the sharp fall in phosphate concentration after the third extraction coincided with the disappearance of the $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ phase, the remaining solid phosphate (equivalent to about 12% of the P_2O_5 originally present), being a more basic salt resulting from decomposition of dicalcium phosphate.

The phosphate concentrations in extracts of the larger weight of dicalcium phosphate dihydrate were also about 0.06 g. P_2O_5 /litre, but successive extracts showed more variation in P_2O_5 concentration than one would expect in a series of extractions of a simple salt. This may have been due to differences in the amount of decomposition occurring in successive extractions. Sanfourche & Henry (loc.cit.) performed a similar experiment with a comparable solid/water ratio, but using a 24 hour extraction period compared with the 30 minutes which we chose as being practicable for our ultimate purpose. They found that the phosphate present in solution as dicalcium phosphate remained more or less constant at about 0.03 g. P_2O_5 /litre, whilst the phosphate simultaneously present in solution as the monocalcium salt was very variable, reaching a maximum of about 0.1 g. P_2O_5 /litre in the 7th extraction. The higher total phosphate concentration found by these authors, coupled with their longer period of extraction, indicates that decomposition of dicalcium phosphate in the presence of water is a rather slow reaction.

After 13 extractions they found that no more monocalcium phosphate appeared in solution, and after 55 extractions dicalcium phosphate was absent, the concentration then being 0.006 g. "tricalcium phosphate" per litre (equivalent to 0.0027 g. P_2O_5 /litre). It is interesting to note that our extractions of hydroxyapatite dissolved 0.002-0.003 g. P_2O_5 /litre.

Looking/

* The figure given by Elmore & Farr for maximum decomposition is that found in a system just saturated with monocalcium phosphate. In the presence of excess solid, the amount of decomposition is a smaller fraction of the total monocalcium phosphate because some of this is present as excess unreacted solid. With the removal of phosphate from solution by plants and by fixation, more solid monocalcium phosphate will be dissolved, and so we can expect that the maximum decomposition will be reached eventually.

Looking further at these authors' results, we estimate that about 30% of the P_2O_5 originally present as dicalcium phosphate remained undissolved when the P_2O_5 concentrations fell to 0.003 g. P_2O_5 /litre, a level which we have assumed indicates that hydroxyapatite was the remaining solid phase. Sanfourche and Henry found that the basicity of the residue was about half-way between that of tricalcium phosphate and that of hydroxyapatite. In our low solid/water extractions we found that the phosphate left undissolved when the sharp decrease in P_2O_5 concentration occurred represented about 12% of the original P_2O_5 , i.e. 24% of the original P_2O_5 had decomposed to monocalcium phosphate and a sparingly soluble basic phosphate. Thus a tenfold increase in concentration of the reaction mixture resulted in less than three times the amount of decomposition.

The relative proportions of fertiliser and water found in soils will vary over a wide range. An estimate which should give the approximate order of magnitude can be made from the available water content of a soil, (i.e. water content at field capacity less water content at wilting point). Data given by Russell (1950) indicate that this varies over the range 0.3-3.0 inches of water per foot of soil, depending on soil type. We can take 1.5 inches as an average figure; this, with a dressing of $CaHPO_4 \cdot 2H_2O$ providing 60lb P_2O_5 /acre distributed throughout a 6 inch depth of soil, gives a value for the dicalcium phosphate/water ratio of 0.9 g./litre. This is comparable with our lower solid/water extractions discussed above.

We conclude, therefore, that the net fertilising value of dicalcium phosphate dihydrate is equivalent to about 30% of the total P_2O_5 as hydroxyapatite and 70% as a "stable" soluble phosphate.

4.1.3. Dicalcium phosphate, anhydrous. As shown in Figure 1 this substance gave a much lower phosphate concentration than did the dihydrate. In this connexion it is noted that Bassett (1908) concluded that the solubilities of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ differed only very slightly. However, because of the extremely slow rate at which the anhydrous salt reacts with or is dissolved by water, this material is commonly taken as having a lower solubility. Although the dihydrate is the stable form below $36^\circ C$. (Bassett, loc.cit.), because of this slow rate of reaction the speed at which $CaHPO_4$ is converted to $CaHPO_4 \cdot 2H_2O$ is so small as to be hardly noticeable.

We have compared the apparent solubility of our dicalcium phosphate with that of a sample of well crystallised $CaHPO_4$, kindly provided by Dr. W.E. Brown of the Research Department, Tennessee Valley Authority. This was slower to dissolve than our material, and a 30 minute extraction contained only 0.007 g. P_2O_5 /litre. After 10 days, with occasional shaking at room temperature, the concentration was 0.013 g. P_2O_5 /litre, compared with 0.015 g. P_2O_5 /litre obtained in the first extract of our sample, both systems having solid/water ratio of 0.5 g. dicalcium phosphate/litre.

The P_2O_5 concentrations in the high solid/water extractions were approximately double these found with the lower ratio. This effect also has been noticed by earlier workers; for example Warrington (1879) found that the solubility of his tricalcium phosphate varied from 1 in 35,000 to 1 in 110,000, depending on the relative quantities of phosphate and water present.

In our successive extractions so little P_2O_5 was dissolved and so little decomposition occurred that we cannot calculate the extent of the latter with any accuracy from the analyses of the residue after extraction. The most that we can do is to state that there is no evidence that the amount of decomposition, relative to the P_2O_5 dissolved, is any greater than for the dihydrate. The differences in apparent solubility of the two substances may result in different rates of availability to a crop; but we cannot, with the data at our disposal, differentiate between them, so far as total availability is concerned.

4.1.4. Hydroxyapatite. Within the limits of experimental error, the P_2O_5 concentrations of these extracts showed no differences due to different solid/water ratios. The results are therefore shown as a single curve in Figure 1. There was a tendency for the P_2O_5 concentration to decrease in later extracts, but by only a very slight amount. As mentioned earlier, the phosphate concentrations in these extracts of hydroxyapatite were in the range 0.002-0.003 g. P_2O_5 /litre. The material used was very finely divided, and its surface development could be expected to change slowly over a considerable period of time. A similar composition which had been aged would therefore be expected to give a solution of lower P_2O_5 concentration.

5.

SCALE OF RELATIVE FERTILISER VALUES

The above results and considerations, together with published data on plant growth tests, enable us to suggest a scale of relative values for mixture of calcium phosphates commonly found in fertilisers. We have chosen monammonium phosphate as a standard because it is a common fertiliser material and is not decomposed by water to give a less soluble phosphate; it can, therefore, be regarded as 100% potentially available.

Ross et al. (1947) assumed that "... the P_2O_5 in the reverted phosphate, and in the undecomposed rock, of ammoniated goods are respectively 50 and 15% available to all crops on acid soils,.....". From our own experience and from a consideration of other published work, Jones & Rehner (1942), Tromblay & Baur (1952), and Martin, Vlaminck & Quick (1953), we believe that these values are rather low. On acid soils we prefer to regard precipitated hydroxyapatite as providing 60% and rock phosphate 20% of potentially available P_2O_5 .

These three points in the scale can then be used to assess mono- and dicalcium phosphates on the basis of their decomposition as discussed above. The scale of values obtained for acid soils is given in Table 4, column 6.

TABLE 4.

Proposed scale of fertiliser values.

Material	Points for soluble P_2O_5	Points for P_2O_5 decomposed		Points for P_2O_5 as rock	Total (acid soil)	Value in calcareous soil
		(a) as dicalcium phosphate	(b) as OH-apatite.			
Monammonium phosphate	100	-	-	-	100	100
Monocalcium phosphate	72	25	-	-	97	93
Dicalcium phosphate	70	-	18	-	88	76
Hydroxyapatite, precipitated	-	-	60	-	60	20
Rock Phosphate	-	-	-	20	20	10

It is common agricultural experience that, whilst there may be little to choose between water soluble phosphate and more basic phosphates on acid soils, the difference between them is much more marked on calcareous soils. We have, therefore, derived a further scale of values applicable to calcareous soils. Ammonium phosphate may again be taken as equal to 100 units on our scale. We have, however, been unable to find sufficient reliable data in the literature of vegetative tests to allow us to fix a point lower down the scale to represent hydroxyapatite. An estimate of this has been made from theoretical considerations, using data given by Aalyng (1954).

He found that the crop yield on a phosphate deficient soil was related to the total phosphate concentration of a solution obtained by extracting the soil with 0.01 M calcium chloride solution. A phosphate concentration of about 2×10^{-6} M in the extract indicated that the soil phosphate was adequate for plant growth. He also showed that the phosphate concentration of such an extract could be used with Bjerrum's (1936) solubility product data to indicate the particular solid calcium phosphate present and responsible for the dissolved phosphate.

were present

If hydroxyapatite in a hypothetical calcareous soil of pH 7.0, we can calculate from the solubility product that the phosphate concentration of the 0.01 calcium chloride extract would be about 2×10^{-6} M. This is only one hundredth of the concentration regarded as optimum for plant growth. It follows that hydroxyapatite is virtually useless for immediate application as a phosphate fertiliser on calcareous soils, although it will have some long-term value in adding to phosphate reserves in the soil. For this reason we give hydroxyapatite a value of 20 on calcareous soils.

Rock phosphate will be even less valuable than hydroxyapatite in such soils because it is likely to be more slowly attacked by water. We believe that a figure of 10 is a fair estimate of its value.

The probable phosphate concentration arising from dicalcium phosphate can also be calculated for this hypothetical calcareous soil and we find that the 0.01 M calcium chloride extract would be about 2×10^{-6} M with respect to phosphate. This is about one hundred times greater than the level which Aslyng believed adequate. There is, therefore, no reason from the viewpoint of solubility for believing that dicalcium phosphate would be less useful on calcareous soils than on acid ones, except for the fraction which is converted to hydroxyapatite. We thus have a value of 76 for dicalcium phosphate in calcareous soils compared with 88 in acid soils.* This value (76) might be an overestimate, because the amount of decomposition of CaHPO_4 is probably affected by the calcium content of the surrounding solution. In a calcareous soil, rich in soluble calcium, it is to be expected that more hydroxyapatite will be produced by decomposition of the dicalcium phosphate than would be the case in a calcium deficient soil. The estimated value of 76 is therefore to be regarded as a maximum figure; later we shall consider how this estimate compares with the results of plant growth experiments.

Owing to the lower value given to dicalcium phosphate in calcareous soils compared with acid ones, the value given to monocalcium phosphate will also be lower, i.e. 93 compared with 97 in acid soils.

The values in calcareous soils are given in Table 4, column 7.

It is interesting to use the solubility product data to estimate the value of hydroxyapatite on an acid soil, and to compare this with the value given in Table 4, which was based on a consideration of the results of plant growth tests. If hydroxyapatite were present in a soil of pH 5.5, and this were/

* An example of the calculation is given:-

Dicalcium phosphate is evaluated as 70% \equiv ammonium phosphate + 30% \equiv hydroxyapatite

i.e. in acid soils $1/100 [(70 \times 100) + (30 \times 60)] = 88$

and in calcareous soils $1/100 [(70 \times 100) + (30 \times 20)] = 76$

were extracted with 0.01 M calcium chloride solution, the phosphate concentration in the extract would be about 1.7×10^{-8} M, i.e. about ten times as much as we believe to be adequate for plant growth. Hence hydroxyapatite would be expected to be as good a phosphate fertiliser on acid soils as a more soluble phosphate, provided that it could be dissolved sufficiently rapidly to maintain the phosphate concentration of the soil solution at or near to the optimum level (i.e. provided that it dissolved to liberate phosphate more rapidly than phosphate was removed from solution by fixation reactions and absorption by plants). Its failure to do this presumably accounts for it being frequently less satisfactory than superphosphate even on acid soils. Under the circumstances the value of 60 given in Table 4, column 6, is probably a fair one.

5.1.

Comparison with plant growth tests

It will be immediately apparent that a set of potential fertiliser values, such as given in Table 4, cannot be expected to agree under all conditions with the results of individual pot trials or field experiments. Such results depend, as mentioned earlier, on a number of variable factors, one of the more important being the choice of test crop. Moreover, the experimental errors of this type of study preclude the possibility of making accurate comparisons between fertiliser materials.

It follows from this that a comparison of our scale of fertiliser values with the results of plant growth tests will neither confirm nor disprove our values but can only give in general terms an indication of their usefulness. With this reservation in mind, it is interesting to compare our values with some results obtained in pot culture studies comparing a number of phosphate materials. Two test crops were used, each being grown both on an acid soil (pH 5.0) and on a calcareous soil (pH 7.6). Table 5 is obtained from the yield increases due to the different fertilisers calculated as percentages of the yield increase due to an equal amount of P_2O_5 as monammonium phosphate. Two of the fertiliser materials have not previously been described; the residue from ammoniated fertiliser was the fraction remaining after a 7 $\frac{1}{2}$:7:2:12 fertiliser had been washed repeatedly with water. At the end of this treatment, the P_2O_5 concentration of the wash water indicated that no phosphate more soluble than dicalcium phosphate remained in the residue. The residue itself contained 10.4% P_2O_5 (4.9% citric-soluble P_2O_5 and 0.3% water-soluble P_2O_5). It was estimated that this material contained about one third of the P_2O_5 originally present in the fertiliser. The nitrophosphate was a conventional product made from phosphate rock, nitric acid, ammonia, ammonium sulphate and potassium chloride. The values of these materials on our scale of relative potential values were estimated by a method to be described in a later section. The pot culture values for each material on each soil are mean figures averaged over the two test crops.

Table 5

Source of P_2O_5	Acid soil		Calcareous soil	
	Fertiliser value averaged over the 2 test crops	Estimated fertiliser value	Fertiliser value averaged over the 2 test crops	Estimated fertiliser value
D.C.P.	68	88	92	76
D.C.P., $2H_2O$	84	88	99	76
OH-apatite	57	60	6	20
Residue from amm. fert.	47	63	64	26
Nitrophosphate	111	80	47	59

It is interesting to note that there is frequently approximate agreement between the estimated values for each material and the mean response of the two crops to that material. We believe that some of the differences between our relative potential values and the yield increase values are due to the difficulty of drawing general conclusions concerning fertiliser values from the results of only a small number of pot tests.

There is no doubt, however, that if the results of a sufficiently large number of plant growth studies could be coordinated, the results thus obtained would be invaluable for assessing the reliability of the scale of values given in Table 4. We emphasise very strongly that we expect at least some of the values will require revision in the light of such future experience.

5.2. Evaluation of mixtures of calcium phosphates, such as are found in fertilisers

The scale of values given in Table 4 can be used to assess the value of a fertiliser based on calcium phosphate provided that its ingredients are known. For example, if a fertiliser were known to contain 75% of its P_2O_5 as monocalcium phosphate, 10% as dicalcium phosphate, 8% as hydroxyapatite and the remaining 7% as unchanged rock, then its potential availability on an acid soil would be:-

$$(75 \times 0.97) + (10 \times 0.88) + (8 \times 0.60) + (7 \times 0.20) = 88$$

On a calcareous soil the corresponding figure would be:-

$$(75 \times 0.93) + (10 \times 0.76) + (8 \times 0.20) + (7 \times 0.10) = 80$$

The difficulty that arises here is in the analysis of a mixture of the calcium phosphates, and it is a problem that we have not yet been able to solve to our satisfaction.

We have, however, been able to get an approximate analysis of such mixtures by repeated aqueous extraction, which permits separation of the constituent phosphate into three groups, depending on whether the solubility, as measured by P_2O_5 concentration in the extracts, is (1) greater than, (2) equal to, or (3) less than that of dicalcium phosphate. Group (1) is assumed to be monocalcium phosphate, and is normally removed in the first two successive extractions; Group (2) phosphate is assessed as dicalcium phosphate, and Group (3) as hydroxyapatite.

However, if much dicalcium phosphate is present, a large number of extractions are needed to dissolve it, and so the method becomes very tedious. Moreover, as the amount of solid dicalcium phosphate remaining decreases, so does the P_2O_5 concentration of the extracts, and it becomes difficult, if not impossible, to obtain a clear-cut division between dicalcium phosphate and hydroxyapatite. As a first approximation, we have assumed that only phosphate giving the required P_2O_5 concentration in the first 12 successive extractions is to be evaluated as dicalcium phosphate, and that phosphate then undissolved is evaluated as hydroxyapatite. This approximation was used to estimate the values of the fertiliser residue and the nitrophosphate given in Table 5.

In practice, the method may be seriously in error only when the basic calcium phosphates (including unattacked rock) comprise the major part of the total phosphate and when the material is evaluated for calcareous soils; for these the value given to dicalcium phosphate is almost four times that for hydroxyapatite, and so any error in the determination of these two compounds will result in a serious error in the estimated fertiliser value.

5.3.

Possible improvements in the method

We have attempted to improve the method of analysis outlined above by successive extraction using a sodium acetate buffer solution at $pH \sim 5.5$ in place of water, after the phosphate of Group (1) had been removed. This had the advantage of dissolving the dicalcium phosphate more rapidly than

did the water, but there was an even greater decrease in P_2O_5 concentration in successive extractions, and it was still not possible to differentiate between dicalcium phosphate and hydroxyapatite. A buffer solution of this type, therefore, has little or no advantage over water as a solvent for selective extraction of the basic calcium phosphates.

It would appear that an essential property of a solvent which could effect this separation is that it should extract phosphate from a particular calcium phosphate in such a way that the P_2O_5 concentration in an extract is independent of the solid/solvent ratio. We have not made any exhaustive search for such an extractant, but a small amount of work on these lines has shown some promising results. This is mentioned here because we do not ourselves expect to carry this work any further, and the results may be of some assistance to other workers in this field.

When a sparingly soluble calcium phosphate is shaken with ammonium oxalate solution, calcium oxalate is precipitated and phosphate is dissolved. Provided that excess oxalate ions are present in solution, the calcium concentration will be very small, as required by the solubility product rule, and in consequence the phosphate concentration is likely to be much greater than in an aqueous solution.

We used a half-neutralised acetic acid/sodium acetate solution, containing ammonium oxalate, as extractant; the acetate concentration was about 0.0025 M, and the oxalate about 0.003 M. The solution which had an initial pH of about 5.0, had little buffer capacity, but it was thought probable that a rather low total salt concentration was more desirable than a high buffer capacity. (This was later confirmed, in that a solution of ten times the acetate concentration was found to be quite unsuitable for the end in view).

Using this solution we found that:-

- (a) The P_2O_5 concentrations in extracts of anhydrous dicalcium phosphate were between 4 and 5 times those in extracts of hydroxyapatite, allowing a distinction to be made between the two materials;
- (b) The P_2O_5 concentrations were almost unchanged for a tenfold increase in solid/solvent ratio (0.08-0.8 g. D.C.P./100 ml., and 0.04-0.4 g. hydroxyapatite/100 ml.);
- (c) In 20 hours' continuous shaking, very little increase in P_2O_5 concentrations was observed over that obtained in 2 hours' shaking, indicating that the systems approached equilibrium quite rapidly;
- (d) The P_2O_5 concentrations of the extracts of dicalcium phosphate and hydroxyapatite were about ten times greater than those of the corresponding aqueous extracts;
- (e) Hydrated dicalcium phosphate gave almost the same P_2O_5 concentration as did the anhydrous salt.

We believe, therefore, that a dilute extractant of this type, containing ammonium oxalate, might prove a useful reagent in the analysis of mixtures of basic calcium phosphates by successive extraction.

SUMMARY AND CONCLUSIONS

(a) A scheme has been proposed for assessment of the potential plant nutrient value of fertilisers based on calcium phosphates. The proposals have for basis the known decomposition of the calcium phosphates in the presence of water. The more basic phosphates decrease in value as the calcium content of the soil solution increases, and so the proposals distinguished/

distinguish between value on acid soils and on calcareous ones. Monammonium phosphate is assumed to have maximum potential nutrient value on our scale.

(b) Materials can be evaluated from their known composition (in terms of monocalcium phosphate, dicalcium phosphate, hydroxyapatite and rock phosphate). Fertilisers of unknown composition may be evaluated from determinations of the P_2O_5 concentrations in not more than 12 successive aqueous extracts, which permit an approximate analysis to be made.

(c) Evaluation in this way may be in error for two reasons: dicalcium phosphate in excess of about 10% of the total phosphate will be evaluated as hydroxyapatite, leading to low values, particularly on calcareous soils. Any rock phosphate present will also be evaluated as hydroxyapatite giving values which are too high.

(d) The system of assessment is not expected to accord with the results of any particular series of plant growth studies, as these are so greatly dependent on the choice of test crop and on other factors. The results of some pot culture tests are given to illustrate this point. However, it is appreciated that the provision of such a scale of values is a first step only, and the system is likely to need modification in the light of future experience, particularly if a sufficiently large amount of data from vegetative tests can be co-ordinated.

(e) Further experimental work is necessary before the assessment can be usefully applied to fertiliser materials of unknown composition which contain considerable amounts of sparingly soluble phosphates; it is particularly important to be able to determine dicalcium phosphate, hydroxyapatite and rock phosphate in the presence of each other. A dilute acetic acid/sodium acetate/ammonium oxalate solution may prove to be a useful extractant for this analysis.

7.

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The work described in this paper was done in the research laboratories of Scottish Agricultural Industries Ltd., Edinburgh, in 1953/54. It is realised that the subject matter could be very controversial, and it is hoped that others will be stimulated to put forward their own considered views.

Concentration of P_2O_5 in successive extracts of
calcium phosphates

