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### SUPERPHOSPHATE AND ITS ALTERNATIVES. FACTORS GOVERNING THE CHOICE

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#### Superphosphate.

It is desirable firstly to say something of the standard material. Superphosphate is the product of the reaction of phosphate rock and sulphuric acid in certain proportions.

As regards the type of phosphate rock which may be used, Gray (1, page 12) says that rock containing less than 26% P<sub>2</sub>O<sub>5</sub> is considered too poor for other than local use, and I doubt whether any rock of P<sub>2</sub>O<sub>5</sub> content appreciably lower than 33% can at present be brought to England to compete economically with Moroccan rock.

JACOB, of the U.S. Department of Agriculture, (2) says that rock containing iron and aluminium in a greater proportion than 5 to 6%  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  is not considered desirable for the manufacture of superphosphate, mainly because of the poor mechanical condition of the product. In spite of these limitations, there is no lack of phosphate rock suitable for superphosphate production, though cost of transport from the nearest deposit is high for many parts of the world. In Britain, we are mainly dependent on Morocco, whose output was 3,708,000 metric tons in 1949 and 4,038,000 in 1950 (3), while the reserves of high-grade ore in the deposit at Kourigha amount to about a thousand million tons (1, p. 75; 4, p. 42).

As normally carried out, superphosphate production requires an acid of concentration close to 70%  $\text{H}_2\text{SO}_4$ . The acid is usually produced by the chamber process. The impurities introduced from pyrites or spent oxide appear to have no detrimental effect on the reaction between phosphate rock and acid, or on the product; even waste acid from refineries etc. can generally be used.

At the time of leaving the den, superphosphate should contain no free sulphuric acid, but about 50% of its phosphorus may be in the form of phosphoric acid, while 20% may remain unreacted. Reaction between these two phosphorus fractions is slow, and becomes slower the more nearly it approaches completion. Storage of superphosphate to allow it to mature is therefore generally necessary, and even after three weeks storage there is about 15% of the phosphorus in the form of free acid, and about 10% unreacted, together with about 5% soluble in citrate solution but not in water, and the remaining 70% or so present as monocalcium phosphate.

The need to store superphosphate and the acidity of the matured product are disadvantages, though perhaps not serious ones. Large storage space would be necessary even if there was no need to mature, owing to the demand for fertilizers being restricted to a few months of the year. The free acid of the superphosphate is often blamed for bag rot and for the caking of mixed fertilizers, but it is not certain that it is the main factor in either case.

To make a ton of superphosphate with say 18% w.sol. and 19.8% total  $\text{P}_2\text{O}_5$  there are needed about 0.595 ton Moroccan rock and 0.365 ton of 100% sulphuric acid. The latter requires say 0.28 ton pyrites, so that the total raw material required for one ton of superphosphate weighs 0.875 ton, 0.125 ton less than the product. This is the basis of one argument for carrying out the production near the market for superphosphate rather than near the points of origin of the raw materials.

The various types of plant used for superphosphate production were described by Mr. Walter Packard (5) in 1937. Since that date the Kuhlmann (6) and Sackett (7) plants have been described. None of these calls for the use of expensive alloys or lead, except for storage and pumping of the sulphuric acid. Process costs and capital charges for the superphosphate plant itself (omitting grinding etc.) amount only to about 10% of the total cost to the manufacturer of producing superphosphate and delivering it to the customer.

Agronomically, no phosphate fertilizer capable of giving better crop yields than superphosphate, when tried over a number of years, seems to have been produced. Thus, A.H. Lewis and Trevains (8), summarising the results of a large number of experiments conducted in Britain in the period 1930-34, on oats, potatoes and sugar-beet, to compare the value of mixtures containing ammonium phosphate with those containing superphosphate, concluded that, for each of the three crops, the average results were almost identical for the two fertilizers. Similarly, in war-time field experiments comparing superphosphate and silicophosphate, Crowther and Cooke (9), with swedes, potatoes and cereals, concluded that there was little difference between the results obtained from the two fertilizers on acid soils, but that superphosphate was the better on neutral soils.

From the results of experiments made in Britain between 1900 and 1940, it has been estimated (10, 11) that the rates of application of fertilizer  $P_{2}O_{5}$  in 1) the South and East of England, 2) Central and Northern England, and 3) the West of England, Wales and Scotland, should be in the ratios 2 : 3 : 5. Whereas the soils of the wetter part of the country are deficient in phosphate, and the use in part of slow-acting fertilizers may be suitable to make up this deficiency, in the drier South-East one is fertilizing for the crop, and superphosphate or other water-soluble fertilizer is especially suitable.

Most of the superphosphate produced in Britain is made up into mixtures, and indeed in 1951 about 60% was used in granular mixed fertilizers (12). Ammonium sulphate is generally used to provide the nitrogen for these mixtures, with muriate to provide the potash. We will deal first with the so-called "dry" mixtures. Owing to the moisture content of the superphosphate, there is around 5%  $H_{2}O$  in the mixture. Some sulphate is present in the muriate, and this and the ammonium sulphate, in the presence of water, react with the monocalcium phosphate, to form mainly monoammonium phosphate and calcium sulphate. This reaction causes caking of the mixture, which has to be put into storage for 2 to 3 months to allow the reaction to proceed sufficiently far so that, when the mass has been broken up, subsequent caking is minimised. "Conditioners" are included in such mixtures to reduce caking still further.

Mixtures containing as little as 30% superphosphate granulate readily, the physical nature of the material being very suitable for this purpose. If muriate only is present with the superphosphate, drying must stop at about 7%  $H_{2}O$  (loss at  $100^{\circ}C.$ ) otherwise hydrogen chloride is driven off. With ammonium sulphate present, however, the free acid is partly neutralised, so that drying can be taken further without evolution of  $HCl$ .

Owing to the free acidity of superphosphate, only small proportions of nitrates should be used in its mixtures. Up to 6% ammonium nitrate can be used in "dry" mixtures, especially if no carbonaceous conditioner is used. In granulation of a mixture containing a nitrate, care would be needed in the drying process to avoid loss of nitrogen in the form of oxides. The position is quite different where the superphosphate is neutralised with ammonia, a subject which will be dealt with at this Conference in a later paper.

Advantages and disadvantages. Summarising the advantages of superphosphate, it is easily and cheaply made from raw materials which, under normal conditions, are readily available in sufficient quantities to satisfy the demand. It lends itself well to the production of granular mixed fertilizers. Agronomically, it is unbeaten as a phosphate fertilizer.

Disadvantages are the need for storage while maturing takes place, and the acidity of the final product; it is suggested that these faults may be less serious than might appear at first sight. The tendency for mixed fertilizers based on superphosphate to form firm cakes due to chemical action is certainly a drawback, though it must not be forgotten that, with some materials, severe caking may take place between crystals of the same substance, ammonium nitrate being a well-known example.

Recently, attention has been concentrated on the amount of sulphuric acid required for the production of superphosphate. For some time, sulphuric acid producers had been changing to the use of American sulphur as their raw material. An increased demand for the element in the U.S.A. resulted in temporary restriction of the amount exported, while it was suddenly realised that known reserves would only last a few more years. This resulted for a time in a very serious position, which however has been eased by a temporary fall in demand for sulphuric acid in several directions, and a partial change to the use of pyrites as the raw material. From the point of view of this country, we have as alternatives to sulphur either pyrites, reserves of which are ample but which has to be brought here from almost as great a distance as phosphate rock; or various indigenous materials, such as gas-works spent oxide, which is in limited supply, or calcium sulphate, conversion of which to sulphuric acid involves a heavy initial outlay and somewhat high production costs.

A disadvantage of superphosphate, which has become increasingly important as the costs of labour and freightage have increased, is its low concentration of  $P_2O_5$ . Calcium sulphate forms roughly half of the total weight; for this the manufacturer gets no payment, while in the majority of cases it is not needed by the crop, so that the whole cost of its handling in factory, store and in the field, of the half bag which it occupies, and of its carriage to the farm, is wasted.

Finally, there is the limitation of the proportion of nitrates which can be used in mixtures based on superphosphate.

## Factors governing the choice.

The choice of a substitute for superphosphate is a very complex matter requiring careful thought, and the material selected may well vary with the circumstances of the individual case.

There are a number of factors, of varying degrees of importance, to be allowed for, such as 1) the relative agronomic merits of the different phosphate fertilizers, which are to some extent dependent on 2), whether the soils of the district are mainly acidic or basic in reaction. Another factor concerning the soil is 3) its content of calcium and sulphur, and possibly of magnesium. Still thinking of the application of the fertilizer, factors are 4) the main crops to be grown, and 5) whether the fertilizer is to be broadcast (by hand or machine) or drilled; bound up with this is the question 6) whether or no the phosphate fertilizer is to be used as part of a mixture with nitrogenous and/or potassic fertilizers, and whether or no granulation is desired. Important climatic factors 7) are rainfall and relative humidity, while temperature has also some importance. Bound up with the last three factors are the relative tendencies 8) of the various phosphate fertilizers, either alone or in mixtures, to take up moisture from the atmosphere and become difficult to distribute in the field.

A most important factor 9) in deciding whether extra expense to produce a more concentrated fertilizer is justifiable is the average length of journey which the products are expected to make. In the same connection, the average length of time which the fertilizer must spend in the manufacturer's store has to be thought of, which leads to 10) a consideration of the relative tendencies of various phosphate fertilizers, either alone or in mixtures, to cake firmly during storage.

The manufacturer wants to know 11) what are the relative unit prices which he can charge for water-soluble, citrate-soluble, citric-soluble, and insoluble  $P_2O_5$ . His choice must also be bound up with his present position and future intentions as regards 12) factories and 13) personnel, particularly on the technical side. In assessing 14) the demand for the fertilizer he wishes to produce he must take account of the amount of basic slag readily available, and its concentration of  $P_2O_5$ .

The readiness of availability of the necessary starting materials 15) will obviously be of importance, including, if "complete" fertilizers (i.e. containing N, P and K) are to be produced, 16) the forms in which fertilizer nitrogen is readily available. An allied question which may be of some importance is 17) whether users will pay extra for fertilizers low in chloride content.

For fertilizers depending on the production of phosphoric acid, there are three extra factors to be taken into account when this is to be made by the "wet" process, 18) the loss of  $P_2O_5$  in the calcium sulphate, 19) the practicability of utilising the calcium sulphate, and particularly of recovering its sulphur content, and 20) the process now being used in the U.S.A. for recovering uranium from "wet" process phosphoric acid.

Finally, the manufacturer must of course estimate 21) the total cost to him of obtaining his raw materials, processing them, selling the product and getting it to the purchaser. A deciding factor 22) in many cases will be the relative costs of fuel, of hydro-electric energy where this is available, and of sulphuric acid.

### Fertilizer application.

Under this heading, the first eight factors of the former section will be considered in some detail. Taking climate first, it has been stated with regard to the U.S.A. (13) that "the big fluctuations which we get in our national production of various crops are usually more closely correlated with the available water supply than with any other single factor." Conditions of bulk storage of a nitrophosphate which may be quite suitable on the continents of Europe or America would result in the formation of a paste if attempted in the high relative humidities of the British Isles. The average rainfall is important in determining not only the type of crops grown and their yields, but also the extent to which the soil is rendered acid by the leaching of lime.

The relative agronomic merits of the different phosphate fertilizers appear to be very dependent on the pH values of the soil, though the effect of pH value varies with the crop, so that it is difficult to get a clear picture. A few recently-published results are given below to illustrate this point.

Martin and others (14) used greenhouse tests with Romaine lettuce, and six California soils known to be acutely deficient in phosphorus, to compare results obtained with normal superphosphate and two superphosphates ammoniated to different degrees. The proportions of the total  $P_2O_5$  which were soluble were as follows:

	Soluble in water.	Soluble in water and ammonium citrate solution (A.O.A.C.)
Superphosphate	92.5	97.8
Lightly-ammoniated superphosphate	62.8	93.5
Highly-ammoniated superphosphate	27.8	93.0

Applications were at the rates of 50, 100, 200 and 400 lb available P<sub>2</sub>O<sub>5</sub> per acre. With four acid soils (loam, sandy loam, muck, and clay loam, of pH values between 5.4 and 5.9) there was no significant difference in the results from the different fertilizers at any level; in other words, the extraction with citrate solution was a good indication of the value of the fertilizer for lettuce plants in these soils. With two calcareous soils, the lightly-ammoniated superphosphate again gave yields just as high as those with ordinary superphosphate. The highly-ammoniated superphosphate however gave much lower yields, and its value varied with the soil and rate of application; with a fine sandy loam (pH value 8.0) a given rate of dressing was equivalent fairly consistently to about 23% of that dressing of superphosphate, while with a sandy clay loam (pH = 7.9) the figure varied from 10% with the lowest to 35% with the highest rate of dressing.

Rogers (15), summarising field trials of nitrophosphates in the U.S.A., stated that, for cotton and cereal crops on soils of the south-east, high water solubility of the P<sub>2</sub>O<sub>5</sub> was not required, but the nitrophosphates of low water solubility appeared somewhat less effective on alkaline soils than was normal superphosphate.

Stanford and Nelson (16), reporting on oats growing in a silty clay loam (pH 6.0), show practically identical grain yields (about 83 bushels/acre compared with 67 without phosphate dressing) whether the fertilizer was superphosphate, dicalcium phosphate or alpha tricalcium phosphate, the dressing being applied at the rate of 40 lb P<sub>2</sub>O<sub>5</sub> per acre. But Olsen and Gardner (17), dealing with sugar beet growing on a calcareous soil (a fine sandy loam), report the following yields of roots, again with fertilizer applied at the rate of 40 lb P<sub>2</sub>O<sub>5</sub> per acre.

<u>Fertilizer.</u>	<u>Tons per acre.</u>
None	13.2
Superphosphate	16.7
Dicalcium phosphate	14.3
Alpha tricalcium phosphate	14.1

G.C. Lewis and others (18) used Romaine lettuce in greenhouse tests on the effects of different phosphate fertilizers in a calcareous soil (pH value 7.8). Whereas superphosphate gave a crop 14 times as great, citrate-soluble tricalcium phosphate only doubled the yield from the untreated soil.

Tremblay and Baur (19) obtained results on plots 60 ft by 6 ft on a soil of pH value 5.8 with crops of five different kinds of vegetable, and using ten different phosphate fertilizers, which seem to show that, even on acid soils, the yields obtained are dependent on the extent to which the P<sub>2</sub>O<sub>5</sub> of the fertilizer is soluble in water, though the phosphate-fixing power of the individual soil and the particle size of the fertilizer are complicating factors. In the accompanying figure, the yield values are for cucumbers, while the solubilities in water of fluorapatite, dicalcium phosphate, monocalcium phosphate and diammonium phosphate are due to W.L. Hill (20).



Coming now to some of the other factors involved in 'fertilizer application,' Cummins (21) and Millar (22) have mentioned the value, for some Australian and American soils, of the sulphur content of fertilizers.

The supply to the farmer of NPK mixed fertilizers is convenient to him, since it reduces his labour costs. It has been suggested (Cunningham, 23) that it leads to bad practice, since phosphate and potash fertilizers are needed earlier in the year than nitrogenous fertilizer. G.W. Cooke (24) however, says that what little experimental evidence there is shows full yields to be obtained by dressings applied entirely at sowing time. The use of nitrogen at a later date for arable crops is not to be recommended except in the case of cereals.

If a mixed fertilizer is required and an ammoniacal salt is to be the nitrogenous component, the choice of the phosphate fertilizer is of course limited, since the use of a basic substance may lead to the loss of part of the ammonia. Similarly, an acidic phosphate fertilizer ought not to be used with a nitrate.

Even in regard to water-soluble phosphate fertilizers, there seems but little advantage agronomically in granulation, though Starostka, Caro and Hill (25) found recently, in greenhouse experiments, that superphosphate gave the best results, with winter wheat, in a sandy loam soil of pH value 4.4, when the particle size was between 8 and 20 mesh, larger or smaller particles giving slightly lower yields. Mechanically, granulation is convenient, minimising caking during storage and blowing during distribution; co-operation with the agricultural engineer is needed to ensure that a suitable distributor is available to the user.

It is well-known that citric-soluble phosphate fertilizers like basic slag need to be finely divided. This has been found true also of dicalcium phosphate (25) When the dicalcium phosphate is intimately mixed within granules with ammonium nitrate, the position is modified; Rogers (15) found that nitrophosphate was more effective in smaller granules (12 to 50 mesh) than in those of larger size, but these figures are not so very different from those noted above for superphosphate.

## Transport and storage.

The above are both of special importance in the fertilizer industry. To make a ton of soluble  $P_2O_5$  in superphosphate, 4.85 tons of raw materials (phosphate rock and pyrites) have to be brought into the country. Supposing that elemental phosphorus was made, from say the phosphate rock of the Montana deposit by means of Canadian hydroelectric power (the cheapest in the world, 26), and sent here to be converted into phosphoric acid, to be used in the production of ammonium phosphate; only 0.44 ton of this material would be needed to make a ton of soluble  $P_2O_5$ .

Storage gains its importance from the seasonal nature of the trade, which is also very important as regards the financing of the industry. To overcome this difficulty, an export trade to distant parts is needed. But to ship one ton of soluble  $P_2O_5$  as superphosphate plus one ton of nitrogen as ammonium sulphate means the transport of 10.4 tons of material. In the form of a mixture of ammonium phosphate and ammonium nitrate, only 4.0 tons have to be moved. With nitrophosphates, intermediate figures would be realised. Where the mixture of ammonium salts was used, gypsum of local origin could supply calcium and sulphur requirements of the crop.

One can visualise in the future a power station in Morocco using atomic energy, and producing elemental phosphorus for despatch to countries within a wide radius.

## The future.

The tendency is for the industry to become more like that of heavy chemicals. In the future, it will use ammonia, phosphoric acid and nitric acid, in addition to sulphuric acid. It is likely to make a variety of products, and to change these from time to time. Its personnel, finance, buildings and equipment will need to be modified accordingly. In order to keep its place in the industry, the individual firm will need to become more interested in research (both in the production and the use of fertilizers) and in technical development. The industry must become more knowledgeable concerning the possibilities before it.

The writer presented a paper which was published last year (27) giving a brief survey of alternative phosphate fertilizers, with special attention to the use of nitric acid. Since then, there has been a useful paper by Mc Knight and others of T.V.A. (28) on the "Partial replacement of sulphuric acid with nitric acid in making superphosphate."

In Fisons Research Department we are seeking to extend knowledge in various directions. Among other matters, we have experimented in the laboratory on the ammoniation of superphosphate, the production of nitrophosphates, and the calcination of gypsum with phosphate rock. A description of this work and the results obtained will be given by Mr. R.F. Knight.

The thanks of the speaker are due to the Directors of Fisons Ltd. for permission to give this paper.

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FIG. 1.

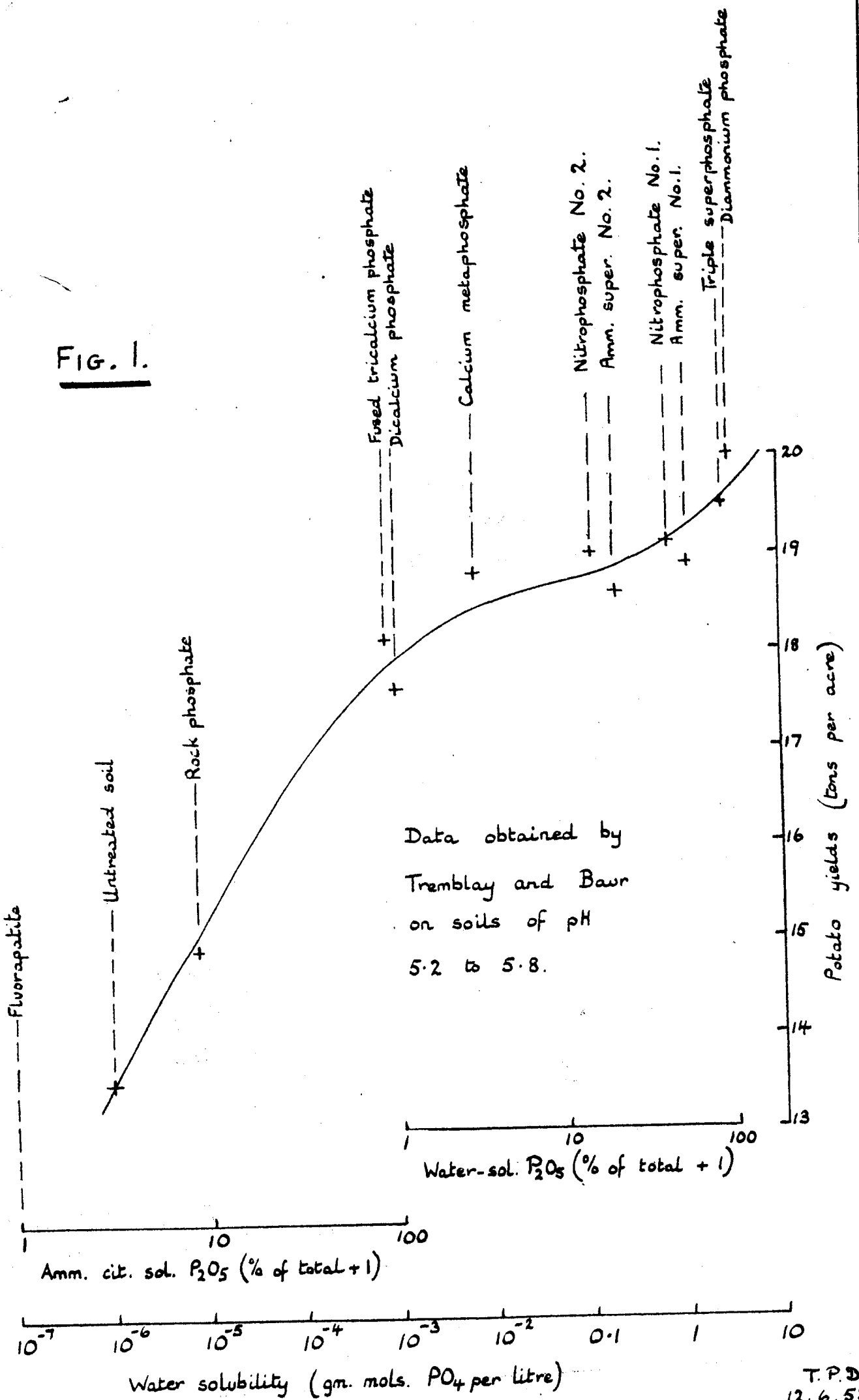
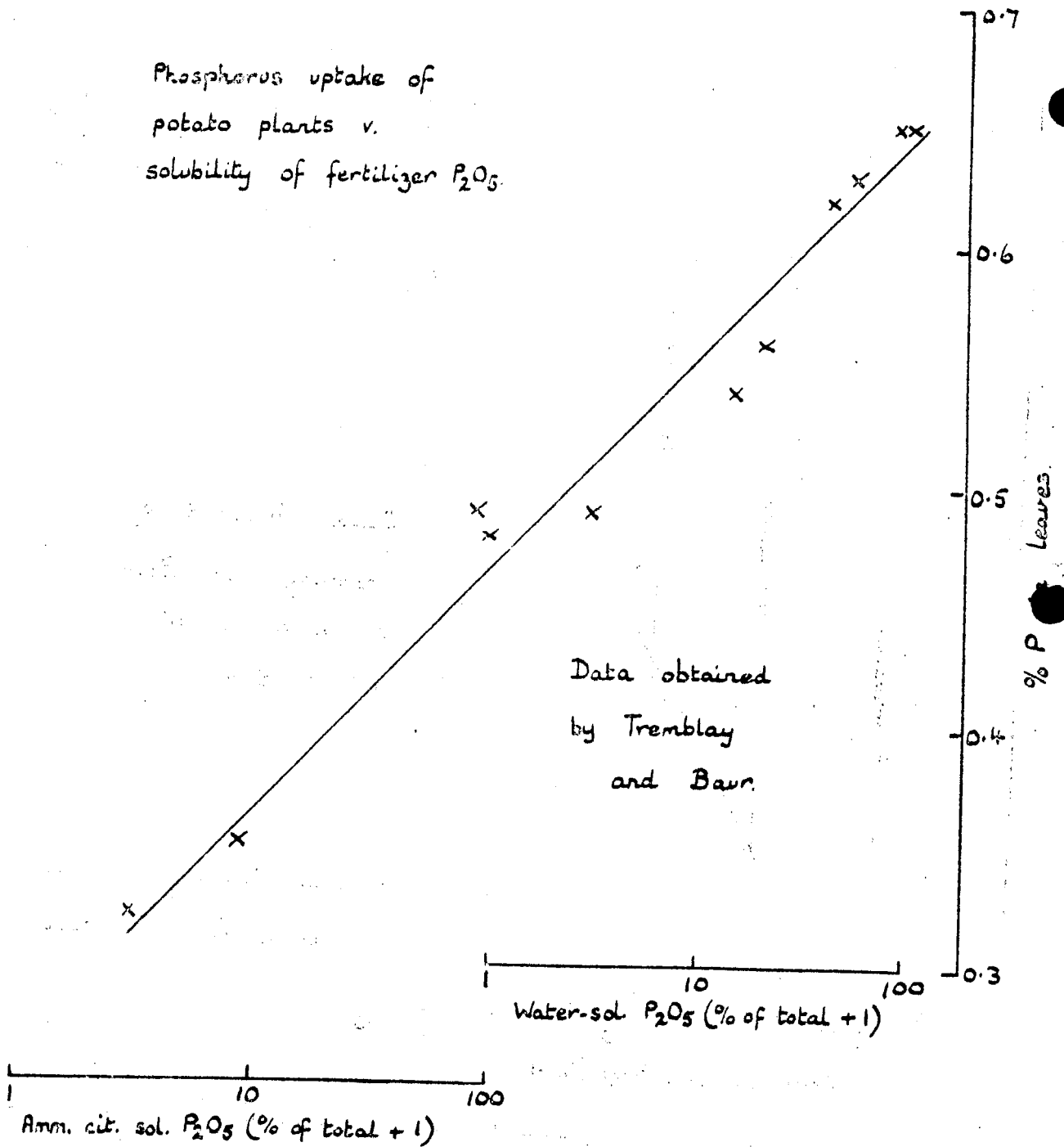


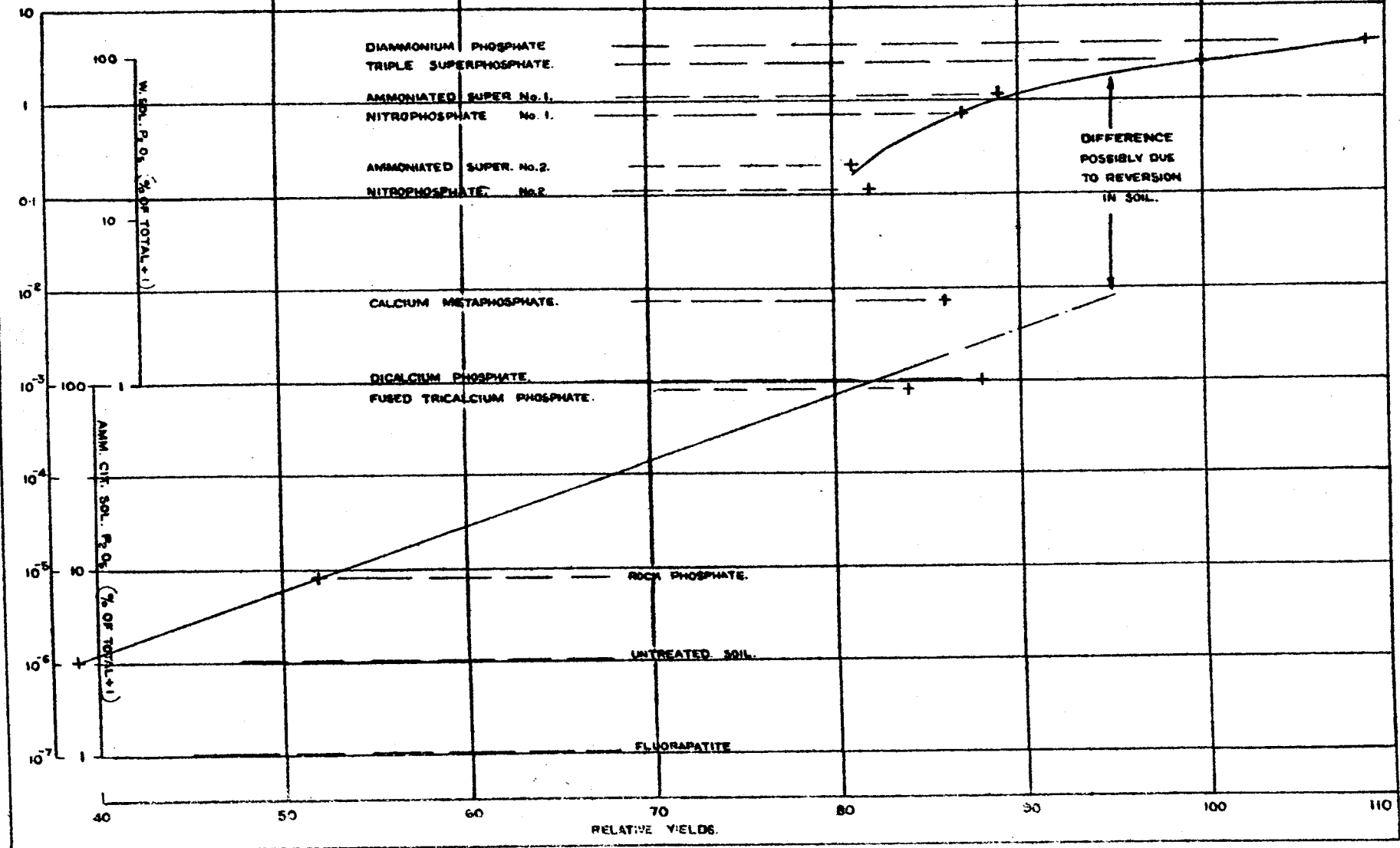
Fig. 2.

Phosphorus uptake of  
potato plants v.  
solubility of fertilizer  $P_2O_5$ .



WATER SOLUBILITY  
(GM. MOLES.  $PO_4$ . PER LITRE)

GROWTH OF CUCUMBERS ON A SILT LOAM, pH - 5.8  
RESULTS OBTAINED BY TREMBLAY & BAUR.



DIFFERENCE POSSIBLY DUE TO REVERSION IN SOIL.

W. SOL.  $P_2O_5$  (% OF TOTAL + 1)

AMM. CIT. SOL.  $P_2O_5$  (% OF TOTAL + 1)

RELATIVE YIELDS.