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ALTERNATIVE PHOSPHATE FERTILISERS CURRENT PROCESSES AND POSSIBILITIES

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The importance attached in high quarters to the problem of replacing superphosphate by other satisfactory phosphate fertilisers is shown by the fact that, along with fuel problems, it was specifically mentioned by Lord Woolton in his welcome to the delegates to last month's international symposium on the Organization of Scientific Research (Anon., 1951a).

What Lord Woolton had in mind was, of course, the present sulphur shortage, and the fact that about 24% of our consumption of sulphuric acid in Britain is for the manufacture of superphosphate (Smith, 1951). Another important reason for wishing to replace superphosphate, however, is its rather low phosphorus content, so that the cost of bagging and of transport to the farm of a given weight of the fertiliser element is a considerable item in these days.

Some of our friends at Rothamsted and elsewhere have seemed to suggest at times that British fertiliser manufacturers have been backward in not having provided at an earlier date a satisfactory substitute for superphosphate. There is, however, much to be said on the other side. The best concentration of sulphuric acid for making superphosphate is one which is readily produced by the chamber process. Although, as might be expected, some technical problems arise in the manufacture of superphosphate, it is essentially a simple matter of mixing the sulphuric acid with phosphate rock, the latter being found in North Africa in such a form that the only preparation it needs is a slight reduction in particle size. Agronomically, no better general phosphate fertiliser than superphosphate is known.

The kind of problem the manufacturer finds himself confronted with can be illustrated by a reference to a process emerging from certain work at the Chemical Research Laboratory, Teddington, and reported by Reynolds to a recent meeting of the Fertiliser Society (1951). I think there can be no doubt, from experience in France and elsewhere, that such a process, involving the partial replacement of sulphuric by nitric acid, would mean that the present superphosphate mixers and the ductwork for removing the acid fumes would have to be replaced by others made of one of the 18-8 stainless steels (Constant, 1951; Crippenden, 1951). Again, the present superphosphate factories are not generally near to nitric acid plants and the cost of transporting the acid at say 55% concentration would be a large item. An investigation would probably show that the product could only be made economically if one or two of the largest superphosphate plants were selected, and nitric acid plants erected next to each of them. By the use of tank cars, the relatively light anhydrous ammonia would be carried to these factories, as is being done in France (Massenet, 1951).

But nitric acid plants mean more stainless steel, and the raw materials for this are as difficult to get as is sulphur. The investment of a large sum of money is called for, and it would probably be at least two years before the plants could be completed.

The manufacturers can only be expected to undertake such an expensive and long-term development if they have clear guidance from the agricultural experts as to the best form of phosphate fertiliser to produce. Until recently we have been assured unreservedly that the water-soluble test for phosphate fertilisers was out of date and ought to be abolished (Crowther, 1945), and that we ought to be considering such processes as the treatment of superphosphate with ammonia (MacIntire, 1944), with the consequent change of its water-soluble monocalcium phosphate to dicalcium phosphate, which is soluble in neutral ammonium citrate solution, as used in the standard American test (Anon, 1950). Just when such guidance would have been welcome, however, there has been a change.

It has been noted in the U.S.A. that citrate-soluble phosphate fertilisers are less effective than those soluble in water on soils with a basic reaction (Waggaman, 1950). Observations made in some experiments, using the radioactive ^{32}P as a tracer, have been interpreted as placing the water-soluble phosphate fertilisers ahead in agronomic value of those needing citrate solution for their dissolution (Parker, 1949). The position now is therefore much less clear, and no one can blame the manufacturers for hesitation.

I will now deal briefly with the various possibilities.

Various Phosphate Fertilisers

Basic slag is very useful as a substitute for superphosphate in certain cases. As a by-product of the steel industry, however, its production cannot be increased at will. Home-produced basic slag supplies about 20% of the total fertiliser phosphorus used in Britain (Anon., 1951b).

Phosphate rock itself (usually the low-grade material coming from Gasfa, in Tunisia), after grinding finely, is used in some areas on grassland, and is being used in certain proportions in some of this year's national fertiliser mixtures. On this, I cannot do better than to quote a recent article by T.W. Walker (1951), of the N.A.A.S. He says: "The results of experiments carried out to compare mineral phosphate with superphosphate and other phosphates are not numerous and certainly not conclusive, but in general it is true to say that on acid soils in the wetter areas ground mineral phosphate can be used profitably on most crops other than potatoes. It is particularly useful on swedes and grassland in such areas. In the drier eastern and south-eastern parts of the country, particularly on calcareous soils, mineral phosphate appears to be of little value for any crop."

The water-soluble phosphate fertiliser, triple superphosphate and ammonium phosphate, depend for their manufacture on the production of phosphoric acid. This is made from phosphate rock either by the use of sulphuric acid or by fusing it with siliceous and carbonaceous matter, usually in an electric furnace (Anon, 1948).

In the latter case, elemental phosphorus vapour issues from the furnace, is condensed from the gas stream, and is later oxidized and hydrated to form phosphoric acid, while a slag consisting mainly of calcium silicate is run off. The requirement of electrical energy is too high for this process to compete in Britain with the sulphuric acid process where fertiliser production is concerned. A modification in which the electric furnace is replaced by a blast furnace was not a success commercially in the U.S.A. (Hill, 1950), but might repay further investigation here if the position arising from the sulphur shortage continues to be so acute.

When made with phosphoric acid from the so-called "wet" process, triple superphosphate requires as much sulphuric acid per unit of phosphorus as does ordinary superphosphate, though it has the advantage of a phosphorus concentration about 2.5 times as high. As regards the ammonium phosphates, the process said to be used by I.C.I. for mixtures containing the monoammonium salt (Curtis, 1932) involves essentially a double decomposition between monocalcium phosphate and ammonium sulphate so that the consumption of sulphuric acid per unit for phosphorus is presumably about the same as for superphosphate.

With commercial monoammonium phosphate, the concentration is about 3.2 times as high as could be attained with mixtures of superphosphate and ammonium sulphate.

Of the fertilisers which require a citrate solution to dissolve them to an appreciable extent, dicalcium phosphate is the most readily soluble. Even so, Hill (1951), of the U.S. Department of Agriculture, has shown, in a recent survey of the relationship between particle size and availability, that this phosphate, when used alone, cannot be expected to evoke a good vegetative response unless applied as a powder. There is a possibility, however, that, in the presence of other salts, granulation may be permissible.

A type of phosphate fertiliser, of which there has been some production in this country under the name of silicophosphate (Anon., 1951c) depends for its production on calcining a mixture of phosphate rock, sand and alkali in a current of steam. The product has similar properties to those of basic slag. Its phosphorus content is about 1.5 times that of superphosphate. It is not suited for use in granular mixtures with ammonium sulphate. Its economic production depends on cheap fuel and a source of cheap alkali. A rather similar material (Hill, 1950) has recently been made in the U.S.A. by fusing phosphate rock with a magnesium silicate mineral in electric furnaces; apart from the cost of electrical energy, our deposits of magnesium silicate are restricted to Cornwall, Anglesey and parts of Scotland (Anon., 1946a).

The Tennessee Valley Authority are producing two fertilisers with their phosphorus in forms which are citrate-soluble. Calcium metaphosphate (Hill, 1950) is a very highly concentrated fertiliser, but for its production elemental phosphorus is needed and can be made only in the electric furnace, as already noted when dealing with phosphoric acid. Fused tricalcium phosphate (Hill, 1950) is made from phosphate rock in an oil-fired shaft furnace, Firing of the furnace with pulverized coal is a possibility, and the process deserves consideration in this country, but the phosphorus content is not particularly high, the material would only compare in effectiveness with superphosphate on acid soils, and even there would need to be used as a powder.

The use of nitric acid.

The use of nitric acid for treatment of phosphate rock to make fertilisers has a number of interesting features. While the nitrogen content of nitric acid is more expensive than that of ammonium sulphate, and its hydrogen content is more expensive than that of sulphuric acid, it replaces both of these in the production of mixed fertilisers, thereby making for a more concentrated and possibly a cheaper mixture.

In some processes it is the practice to use sufficient nitric acid to form phosphoric acid in the slurry, then to add ammonia in such a proportion that dicalcium phosphate is formed. The ammonia is held in the final product in the form of ammonium nitrate, and this would result in an increased saving of sulphuric acid in a country where ammonium sulphate would otherwise be made from synthetic ammonia and sulphuric acid. Since our synthetic ammonia is almost all reacted with anhydrite to make ammonium sulphate, this extra saving would not occur in our case.

It is of course possible to make a fertiliser similar to superphosphate by the action on phosphate rock of nitric acid (Reynolds, 1951; Volfkovich, 1949) with or without sulphuric acid. The product has its phosphorus mainly in a water-soluble form, and has a considerable content of free acid. It would probably need to be cooled during the manufacture to minimize the evolution of oxides of nitrogen during storage in large quantities, but might be suitable for direct application to the land if it did not corrode the drills too badly. However, about 60% (Anon., 1951d) of the superphosphate made in this country is used in the production of granular mixed fertilisers. We have found that such mixtures, made with an acid nitro-phosphate, need careful drying at a low temperature to minimize loss of nitrogen.

The following equations indicate that, if phosphate rock is treated with the correct proportion of nitric acid to make phosphoric acid, and the resulting slurry is treated with the correct proportion of ammonia, the final slurry being then granulated and dried, the product is a mixture of dicalcium phosphate, ammonium nitrate and calcium nitrate. Unchanged phosphate rock, calcium fluoride and other impurities from the phosphate rock are also present:

$$(1)\quad P_2O_5,3.4CaO + 6.8HNO_3 \dashrightarrow 2H_3PO_4 + 3.4Ca(NO_3)_2;$$

$$(2)\quad 2H_3PO_4 + 3.4Ca(NO_3)_2 + 4NH_3 \dashrightarrow 2CaHPO_4 + 1.4Ca(NO_3)_2 + 4.0NH_4NO_3$$

Such a product is neutral and chemically stable; the general opinion, however, is that the presence of calcium nitrate makes it too hygroscopic for general use as a fertiliser. Various processes have therefore been developed to eliminate or reduce the calcium nitrate content.

In some of these processes, part of the calcium nitrate is removed by cooling the acid solution until crystallization occurs, the residual solution being ammoniated and the resulting slurry granulated and dried (Plusje, 1951). Calcium nitrate is thus a by-product of the process. Unless nitric acid of a high concentration is used, and production of this is rather costly, refrigeration is necessary to separate sufficient of the calcium nitrate, and this is expensive. The capital cost of the plant is also likely to be high. Such processes may be suitable where there is a large demand for calcium nitrate as a fertiliser, but even so, there is the difficulty of keeping the sales of two products in balance with one another.

The presence of calcium nitrate in the product may be avoided by using sulphuric or phosphoric acid (Quanquin, 1947; Houston, 1951; Anon.,1946b) together with the nitric acid. For instance, one might have:

$$(3)\ P_2O_5,3.4CaO + 6\ HNO_3 + 1.4\ H_2SO_4 + 6\ NH_3 - 2CaHPO_4 + 1.4\ CaSO_4 + 6NH_4NO_3$$

In the British fertiliser industry, we have an ample production of ammonium sulphate from synthetic ammonia and anhydrite. It is logical to make the most of any new nitric acid plants, and to produce to maximum quantity of mixed fertiliser with their aid. Operation according to the following equation minimizes the consumption of nitric acid, and does not call for any sulphuric acid:

$$(4)\ P_2O_5,3.4CaO + 4.8\ HNO_3 + 1.4(NH_4)_2SO_4 + 2NH_3 - 2CaHPO_4 + 1.4CaSO_4 + 4.8NH_4NO_3$$

Incidentally, in this case, monocalcium phosphate is formed initially instead of phosphoric acid.

Apart from the saving of acid, a further advantage over operation according to equations (2) or (3) is that the heat of ammoniation is less, so that excessive temperatures can more easily be avoided. I.C.I. (Anon., 1951e) have described a process of this nature.

The initial products of such processes are slurries which can be granulated by the addition of a suitable proportion of fine material separated from the final product; after this, the granules are dried in a rotating drum. Extra ammonium sulphate and/or muriate of potash can be added during the granulating process to give the various NPK ratios which are called for.

The fertilisers thus produced are sufficiently non-hygroscopic to be stored safely in the five-ply paper sacks which are becoming the standard package in the industry (Brook, 1950), and can apparently be distributed in the field without trouble if reasonable precautions are taken. So far as present experience goes, there is no great trouble with caking during storage.

As to their agronomic value, it is a good point that their nitrogen content is partly in the form of NH_4 and partly as NO_3. The French evidently have no doubts as to the vegetative response to the phosphate content, since under the Monnet plan they propose to convert 50% of their production of fertiliser phosphorus to the manufacture of these so-called "complex" fertilisers (Massenet, 1951). In the U.S.A., it seems from the previously mentioned article by Hill (1950) that there is some doubt as to the crop response when these fertilisers are applied in granular form, and one gathers that our own agricultural experts have the same feeling.

Whereas available phosphates are of special value in the seed-bed, the need for nitrogen increases as the plant grows, and it has been suggested that, instead of applying a mixed fertiliser to the seed-bed, the phosphate should be applied then and the nitrogen in subsequent dressings (Cunningham, 1951). In view of the convenience and saving of labour in using granular mixtures, I suggest that a useful compromise would be to apply the phosphorus and potash, with a portion of the nitrogen, in this form, and the remainder of the nitrogen, perhaps as ammonium sulphate, as a later dressing.

According to equation (4) the initial product has a weight ratio N: P_2O_5 of 0.95. If it were desired to reduce this, the logical method would seem to be the use of phosphoric acid, mixed with the nitric acid. Thus it may be possible to realize the equation:

$$(5)\ P_2O_5, 3.4\ CaO + 3.4\ HNO_3 + 1.4\ H_3PO_4 + 3.4\ NH_3 - 3.4\ CaHPO_4 + 3.4\ NH_4NO_3$$

This gives a product with an N: P_2O_5 weight ratio of 0.4, in a highly concentrated form. If extra phosphoric acid and ammonia were used in the proportions for diammonium phosphate, the same N: P_2O_5 ratio would be maintained, but with some water-soluble phosphate and an even more highly concentrated fertiliser. If the later nitrogen dressing were given as ammonium sulphate, the sulphur requirements of the plant would continue to be satisfied.

By the above methods granular fertilisers (NP or NPK), of good physical properties and of chemical composition variable within wide limits, can be made from phosphate rock, anhydrous ammonia, nitric acid, phosphoric acid, ammonium sulphate and muriate of potash, without the handling and storage of an intermediate solid product, as in the case of superphosphate. No maturing period would be necessary, and storage could be in bags or in bulk as convenient, though in the latter case it might be desirable to operate a drying plant on damp days to keep the relative humidity of the atmosphere in the store below 80% or so.

Although the agronomic position needs to be clarified before any heavy expenditure takes place, the possibilities of the use of nitric acid (with or without phosphoric acid) seem so promising that intensive development work in the pilot scale is desirable, since such work is likely to take something like two years for its completion.

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