ISMA* Technical Conference

Stockholm, Sweden
14-18 September 1959

*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

TECHNICAL MEETINGS - STOCKHOLM

MANUFACTURE ON A KUHLMANN CONVEYOR OF TERNARY FERTILISERS BASED ON SUPERPHOSPHATE

by P. DONDIN
Etablissements Kuhlmann

This manufacture appears as the logical extension of that of superphosphate. It may be envisaged most simply as the incorporation of salts of fertilising elements with super-phosphate while still on the conveyor. But attempts to do this have not turned out successfully, partly due to lack of homogeniety of the fertiliser so produced and partly by reason of the delaying of the reaction consequent on the addition of salts to the hot superphosphate.

The essential idea which has permitted the development of the process is the putting together of all the constituents at the mixing (kneading) stage, as in the case of superphosphate.

The conditions required for this continuous manufacture, which gives a quick set in the fertiliser, are very different from those which are suitable for batch manufacture in dens.

They have enabled the preparation of a fertiliser of almost perfect homogeniety with a substantial economy of sulphuric acid. The characteristics of this fertiliser are sufficiently similar to those of superphosphate to enable the conveyor installation and the associated plant to manufacture either product without modification.

The materials primarily employed the mutual combinations of which have so far been investigated, are :

- Sulphuric Acid
- Phosphates, Moroccan 70 and 75% and Tunisian 65%
- Liquid ammonia
- Muriate of potash
- Sulphates of ammonia and potassium

The complexity of the chemical reactions possible under these conditions implies necessarily a choice of formulas, but it soon becomes apparent that there exists only one truly chemical restriction limiting the equilibrium between the fertiliser elements: the avoidance of the evolution of hydrochloric acid when employing potassium chloride as the source for potash.

On the other hand, the necessity of obtaining a solid fertiliser within a relatively short time (between 10 and 20 minutes) leads to the imposition of very precise physico-chemical characteristics on the raw materials, which in turn determine the conduct of manufacture and the choice of certain formulae in preference to others which are similar but more difficult to manufacture.

All possible combinations of these products have not yet been tried, either because they are not agronomically attractive (low content of one of the elements) or because technical considerations and the agricultural economy of the area of distribution of such fertilisers, have not justified their appearance.

It can be said, however, that the process has been tested for formulae giving grades 1 / 2 / 2 and 2 / 2 / 1 with a total of soluble fertiliser elements lying between 20 and 25%.

PRINCIPLE OF THE PROCESS.

For more than 10 years fertilisers of similar type have been manufactured by a batch process, by mixing charges of a mixture of ground phosphate and muriate of potash with sulphuric acid partially saturated with ammonia.

The problem was to retain the advantage of this process (direct utilisation of liquid ammonia to form sulphate of ammonia in situ from the acid of the mixture, and the preliminary mixing of the solid constituents) while coping with the quick set on a superphosphate conveyor and continuous mixing of all the constituents.

The result was obtained :

1). by controlling the fineness of the solid mixture at its optimum value for a quick set,

2). by continuous manufacture of the ammoniated acid in a packed column and by regulating its concentration and temperature.

The following observations are to be made :

The attack of a solid mixture containing muriate of potash was effected without evolution of hydrochloric acid while the first acidity of the sulphuric acid remained saturated in the ammoniated acid employed. It is undesirable for HCl gas to be produced as this occurs at the mixer stage and consequently leads to corrosion.

The attack of the phosphate rock by the second acidity (ammonium bisulphate) can be extended to about 85% of the total water-soluble P_2O_5. The decomposition of the fluorine salts of the phosphate is very slight.

The ammonium bisulphate does not behave as a mixture of equal parts of sulphuric acid and neutral sulphate during the attack of the phosphate. A variable proportion of the

bisulphate reacts according to the theoretical reaction:

(1.) $3 \, NH_4HSO_4 + Ca_3(PO_4)_2 \longrightarrow 3 \, CaSO_4 + (NH_4)_2HPO_4 + NH_4H_2PO_4$

The importance of this reaction in relation to the main overall reaction :

(2.) $4 \, NH_4HSO_4 + Ca_3(PO_4)_2 \longrightarrow CaH_4(PO_4)_2 + 2 \, CaSO_4 + 2(NH_4)_2SO_4$
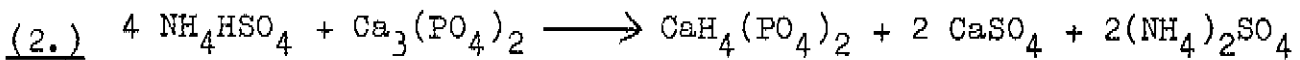
is determined by the ratio between the available free acid in the form of bisulphate and the total P_2O_5 of the phosphate. If they are present in the proportions required for an attack similar to that normally sought in a superphosphate, reaction (1) apparently does not occur.

If there is a deficiency of free acid in relation to the P_2O_5, reaction (1) occurs to make good up to almost one third of this deficiency.

The practical conclusions resulting from these observations are as follows :

If one employs the muriate as the source of potash, one must allow at least 50% for the nitrogen (expressed as N_2) relative to the water and citrate soluble P_2O_5 (expressed as P_2O_5) in the desired formula.

For the same degree of solubilisation of P_2O_5 a saving of 5 to 15% sulphuric acid is achieved compared with an identical formula produced by mixing superphosphate and salts.

Lastly, in order to be complete, we must mention that if potash is introduced as the muriate, there is a double decomposition between the ammonium sulphate.

Such are the basic facts. Their interpretation enables us to employ different phosphate rocks or to replace part of the ammonia by sulphate of ammonia mixed with other solid constituents, or else to introduce the potash as sulphate.

CONTROL OF RAW MATERIALS FOR THE MANUFACTURE OF FERTILISERS ON THE CONVEYOR

The control arrangements aim to obtain crystallisation of the calcium sulphate in the form of anhydrite, at the latest within 20 minutes of the fertiliser leaving the mixer.

The factors affecting this phenomenon are many and difficult to distinguish clearly by reason of their inter-reaction and also because of the peculiar nature of the phenomena of crystallisation which will sometimes maintain a crystalline form outside the normal zone of stability either through inertia or previous seeding.

CONDITIONS REQUIRED FOR THE AMMONIATED ACID.

The most important is temperature, which is tied to the actual temperature of the reaction. Four temperature zones may be distinguished, - of which two are favourable and two unfavourable.

First, there exists a temperature threshold below which the rate of attack is too slow. The temperature of the ammoniated acid must enable this threshold to be exceeded. For this reason, when starting up, especially in winter, it is necessary to use an acid 15°C above the normal process temperature.

In general, for ternary fertilisers, the operating temperature must rise in proportion to the required nitrogen content. It is thus fortunate that the properties of the ammoniated acid are such that, with the same content of water, it will crystallise at a temperature which rises with increasing nitrogen content.

Subsequently, we reach a temperature where the attack is too rapid which causes the product to harden while still in the mixer and risks blocking it. This temperature, like the first, is influenced by the fineness of the solid mix - the finer the grind, the lower the temperature. It lies about 20°C above the working temperature, thus delimiting the first useful setting zone for the fertiliser.

If the temperature of the ammoniated acid is still further increased, we reach a zone in which no set occurs (that is, not in less than 8 - 16 hours).

Experience shows that we then get simultaneously a slowing of the attack and very slow crystallisation of the elements in very compact form. If the fertiliser is artificially cooled it crystallises very well, but there remains a large amount of ammonium bisulphate which is no longer reactive, and the solubilisation of the P_2O_5 is very poor.

Lastly, we have been able, in some cases to show a second setting zone at a high temperature (above 135°C) where the ammoniated acid is employed at boiling point, but its practical interest is slight in view of the attendant difficulties.

The second important factor in using the ammoniated acid (apart from the nitrogen/SO_4 ratio, which depends on the required formula) is its water content.

We must not stress this too much, for in practice it is a factor that we cannot vary too freely. Too much water lowers the concentration of the fertiliser and too little makes the handling of the ammoniated acid impossible: it becomes too viscous and crystallises too quickly in the zone of the diagram of the ternary system H_2SO_4/NH_3/H_2O which embraces the normal ammoniated acids. It has been observed however, that a satisfactory set occurs only between two water contents of the ammoniated acid and these limits vary according to the particular fertiliser which is being manufactured.

CONDITIONS TO BE FULFILLED FOR SOLID MIXTURES

The Phosphate rock and the salts here play quite different roles. For the rock the rule is the same as for superphosphates: the finer the grind, the quicker the set and, therefore, in theory, the better the reaction goes, although risk of blocking the mixer is likely if the fineness is excessive.

In general, it can be taken that grinding to a residue of 18% on a mesh of 0.08 m/m and 8% residue on a mesh of 0.16 m/m ensures good flexibility of operation in relation to the other variables.

The behaviour of the salts in the reaction is not what one might expect from their usual physical properties: the sulphates do not give a better set than the muriate of potash - rather the reverse.

In principle, to ensure a homogeneous mixture, we try to obtain the salts at the same fineness as the phosphate, and in general, the fineness of the salts also appears to contribute to the set of the fertiliser on the conveyor, but to a much lesser extent than the phosphate.

We have not had any trouble from the anti-caking agents (stearates) used at less than 1 part per 1,000 in muriate of potash to prevent its caking.

OPERATION OF THE PROCESS

Preparation of the ammoniated acid.

Ammoniated acid is produced continuously in a lead-lined counter-current column, the acid entering at the top and the ammonia at the base.

To dissipate the excess calories, which would normally lead to a temperature of $130°$ to $160°C$ for the ammoniated acid, the acid leaving the column is cooled and part is recycled to stabilise the flow.

It has not previously been possible to find a physical method of controlling the strength of the ammoniated acid, which could be used to control the operation automatically.

The control of the concentration of the three materials: free acid, ammonia and water, is effected by chemical means and once the working conditions are established, control of manufacture is effected by adjusting the ammonia feed, measured after the stop valve, to the temperature of the acid leaving the column. Periodic checks of the strength are then made to verify the constancy of the other variables.

For a conveyor producing 20 tons per hour of super – phosphate, which produces 15 tons ternary fertiliser per hour, two ammoniating columns each of 4.5 metres high and 1.1 metres diameter are necessary.

It appears that one restricting element in the process is the need to control the temperature of the ammoniated acid between its production and its utilisation, to avoid risk of crystallisation.   There must be a buffer stock of ammoniated acid in a tank, and it is necessary to absorb this entirely each time manufacture is stopped, for this acid crystallises, according to its strength, between 40 and $70°C$.

Studies are proceeding to work out a process allowing us to dispense with the buffer stock of ammoniated acid.

The fixation of the ammonia is practically 100%, so that the effluent leaving the columns is composed of water vapour, voided direct to the atmosphere.

Preparation of the solid mixture

Usually the solid product is prepared in an automatic weighing and mixing machine , ground in a pendulum mill and transported pneumatically to the conveyor manufacturing plant.

In relation to the preparation of ground rock for superphosphate, the only particular points which differ are the preliminary mixing and the finer grind.   The most usual mixtures are of two constituents: phosphate rock and muriate of potash.

It might be advantageous to mix after grinding/the case of ternary mixtures.

Modifications to the actual conveyor manufacturing plant

The only real modification is to the mixer paddle

which has been adapted for fertiliser manufacture.

Other modifications are merely adjustments, fitting suitable gears to the control of the gauge and weighing machine (adjustment of feeds) and regulating of the speed of the conveyor to obtain the optimum retention time.

The conveyor feed can deliver from 8 to 15 tons fertiliser per hour.

RESULTS OBTAINED

The fertiliser leaving the conveyor has a free acidity between 3 and 5% and a moisture content of 8 to 11%.

Its appearance is similar to that of a superphosphate made from the same type of rock as that used in this fertiliser, but with a higher proportion of small lumps: in fact, it is not so much powdered as cut up by the disintegrator.

Maturing in heaps requires 3 to 4 weeks, i.e. double that required for a superphosphate. During this time its free acidity falls about 2 to 2.5% and its moisture content 2 to 3%.

Its behaviour in the heap is about equal to that of a superphosphate manufactured by the old batch type den, that is it is hard enough to require the use of a mechanical type scraper, while superphosphate made on the conveyor can be recovered from the heaps, simply by means of an automatic shovel.

Its perfectly homogeneous appearance is an appreciable advantage, not only for the powdered grade but also, and above all, for granulation: there is no need to screen the fertiliser during granulation.

During the three years during which this process has been employed, the installation for manufacture on the conveyor in question has produced about 60,000 tons of fertiliser, mainly of the formula:

    5 parts nitrogen from ammonium sulphate (in the form of sulphate, phosphate and chloride)

    10 parts total P_2O_5, of which 8 parts are water and citrate soluble.

    10 parts soluble potash from the muriate (in the form of sulphate and chloride)

An example of the chemical analysis of such a fertiliser is given:

| | Water | P_2O_5 | | | Nitrogen | Potash |
	H_2O	free	water soluble	water + citrate soluble	Total	N_2	K_2O
As manufactured (24 hours)	8.9	1.7	7.0	7.4	10.9	5.1	10.1
As despatched (4 weeks)	7.4	0.6	7.4	8.2	10.8	5.1	10.3

An installation for dish granulation is in course of erection to complete the plant for manufacture on a conveyor of either superphosphate or compound fertilisers.

Trials have been made on a pilot-plant at one-tenth scale and have enabled us to determine the conditions under which ternary fertilisers manufactured on the conveyor may be granulated by this process, like superphosphate, immediately on leaving the conveyor.