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REFLECTIONS ON THE EVOLUTION OF FERTILISERS - COMPOUND FERTILISERS

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At a time when a great number of organisations in many countries are interested in the question of compound fertilisers, it might be advisable to define the governing principles, on which the evolution of such fertilisers is based, which should preoccupy, on the one hand, those who guide this process of evolution and perfect methods and, on the other hand, those who are entrusted with the modernisation of means of their exploitation.

Most of those who have studied this question believe that such evolution of compounds has taken place and will continue to take place on the basis of economising in the use of sulphuric acid.

Personally we think that this is a mistaken opinion. It is probable that it was correct at the outset many years ago, but comparative studies of the cost price have very quickly shown that the chief profit-making element in the manufacture of compounds was not the economy in sulphuric acid but the economy in the cost of manufacturing and handling the intermediary products. In consequence it was necessary to guard against offsetting economies in sulphuric acid by an increase in expenditure, which might be at least equivalent to the costs of manufacture of the compounds, and which are due to the increasingly complicated process of manufacture.

Even though the manufacture of compounds, whether by means of a sulpho- or phospho-nitric attack, has seen a simplification of the methods of attack, together with an economy in sulphuric acid, it does not necessarily follow that the search for further economy will be accompanied by a similar simplification. On the contrary, the reverse should be expected.

It might be interesting to work out how the minimum cost prices are related, but local conditions have too much bearing on the calculations to lay down a general rule, and everybody should study this question on his own account.

What is certain is that the low cost price of sulphuric acid is of little consequence when compared with the cost of manufacture of the intermediary products, which have been suppressed in the technique evolved in the manufacture of compounds, or with the growing complexity of these compounds.

In these circumstances it is easy to understand that the Cie de Saint-Gobain has been guided by the principle of rendering the best service to agriculture and incidentally achieving the lowest cost price in its researches into fertilisers.

These principles have been followed by us in the manufacture of compounds under a sulpho, or phospho-nitric attack, as well as in the granulation of Superphosphate leaving the den without handling or drying.

The manufacture of compound fertilisers is dealt with hereunder, whereas the manufacture of granulated Superphosphate will form the subject of a separate paper.

Under the same heading can be classified the manufacture of fertilisers of a purely ammoniacal type, as for instance 4.10.10, granulated, with manufacture in situ of the sulphate of ammonia.

This manufacture too is carried out with a small economy in acid, but the important factor here is the economy effected in the manufacture and the handling of ammonium sulphate, and in the granulation which takes place without drying.

If the guiding principle is an economy in manufacturing costs and the costs of handling intermediary products the manufacture of which is unnecessary, there is no doubt that sooner or later this will result in compound fertilisers which are cheaper than the equivalent straight fertilisers and this is we assert, the aim which everyone should seek to achieve.

Granulated Compound Fertilisers

In September 1951 Mr. Martin submitted a paper on the manufacture of fertilisers by means of nitric-solubilisation of phosphate. He gave a general summary of the different methods, using the solid and the liquid phase and stressed the economies effected in the use of sulphuric acid.

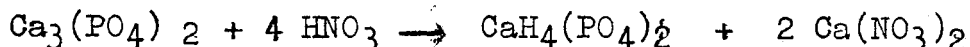
Since then numerous industrialists in different countries have taken an interest in the methods, using the so-called liquid phase, especially in view of the economy in sulphuric acid which this made possible, a most important factor in that period of sulphur scarcity. Plants have been constructed, experiments have been started and followed up, and it may now be said that several processes have proved themselves over several years of industrial use.

Principle of Processes

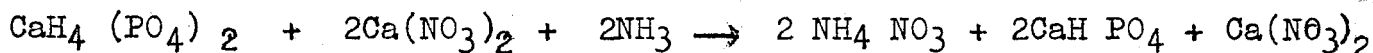
Let us sum up the general principles which are usually followed.

In essence the processes confine themselves to the following theoretical stages:

1. Nitric attack of tricalcium phosphate to obtain a slurry of calcium nitrate and monocalcium phosphate:



2. Ammoniation of slurry to produce dicalcium phosphate



As may be seen, one molecule of the calcium nitrate remains unattacked.

3. Elimination of the unattacked calcium nitrate molecule according to the following processes:

- (a) $\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4 + 2\text{NH}_3 \rightarrow 2\text{NH}_4\text{NO}_3 + \text{CaSO}_4$
- (b) $\text{Ca}(\text{NO}_3)_2 + \text{H}_3\text{PO}_4 + 2\text{NH}_3 \rightarrow 2\text{NH}_4\text{NO}_3 + \text{CaHPO}_4$
- (c) $\text{Ca}(\text{NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O} + 2\text{NH}_3 \rightarrow 2\text{NH}_4\text{NO}_3 + \text{CaCO}_3$
- (d) $\text{Ca}(\text{NO}_3)_2 + \text{K}_2\text{SO}_4 \rightarrow \text{KNO}_3 + \text{CaSO}_4$
- (e) $\text{Ca}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{SO}_4 \rightarrow 2\text{Na}_4\text{NO}_3 + \text{CaSO}_4$
- (f) elimination of $\text{Ca}(\text{NO}_3)_2$ by filtration.

4. Ultimate addition of potassium salt to obtain a ternary fertiliser.

In the above description we have simplified the formulas by not taking into account the molecules of water and of fluorine compounds, so as to have a clearer picture of the processes.

Practice of Processes

We have retained the following procedures, some of which have been utilised industrially.

- (a) Attack of unground phosphate by sulphuric and nitric acids, introduced simultaneously into the reaction chamber; first, there is a formation of monocalcium phosphate; then ammonia is introduced which produces a neutral slurry containing dicalcium phosphate, ammonium nitrate and calcium sulphate. The procedure then calls for a thickening of this slurry by the addition of finely ground finished material, and finally of potassium salt (generally chloride); it is then necessary to granulate and dry the product, which is passed on to a separator with two screens, to obtain the marketable granule; the oversized granules are pulverised and returned to the neutral slurry.
- (b) The same method as above, but using, instead of sulphuric acid, phosphoric acid or a mixture of phosphoric and sulphuric acids.
- (c) Attack of phosphate by nitric acid, then ammoniation. The solution is then filtered to eliminate the dicalcium phosphate. This solution which contains calcium nitrate is treated with ammonia and carbonic dioxide to obtain ammonium nitrate and carbonate of lime. The reaction product is filtered to separate the carbonate in the ammonium nitrate.
- (d) Attack of phosphate by nitric acid, then an addition of sulphate of ammonia. The calcium nitrate is thereby converted into ammonium nitrate and calcium sulphate. The slurry is filtered to eliminate the calcium sulphate which has been precipitated. The sulphate is attacked by ammonium carbonate which is used in manufacture; the acid liquor is neutralised by means of ammonia. To this is added potassium chloride and the product is granulated and dried by the usual method.
- (e) Attack of phosphate by nitric acid, then, after cooling, separation of calcium nitrate by filtration. The acid liquor, containing monocalcium phosphate, is treated with ammonia to obtain dicalcium phosphate and ammonium nitrate. The addition of potassium salt gives a compound fertiliser. A variation of this process consists in separating the nitrate of lime, not alone, but with ammonium nitrate in the form of a double salt.

The fertilisers produced by means of these processes have one thing in common: the phosphate of lime is in the form of dicalcium phosphate. As a result an economy in acid is effected; obviously only half the quantity of acid is needed to render soluble phosphate in the form of dicalcium phosphate, as compared with phosphate in the form of monocalcium. In certain formulas, with a high P_2O_5 figure one part of assimilable P_2O_5 is in the form of ammonium phosphate. The fertilisers are generally granulated owing to the fact that they go through a liquid phase.

Choice of a process:

The basic problems which interest the manufacturers are the following:

the possibility of producing in the same installation very varied formulas to meet the present and future demand;

reduction of the machinery and especially reduction of the weight of stainless steel;

reduction of working costs (maintenance, fuel, loss in raw materials, nitrogen especially.)

In judging a process, these three factors must inevitably be taken into consideration.

The choice of process must depend on the following considerations:

1. Fertiliser market - to give an instance, the market for nitrate of lime is in certain countries extremely restricted, and the process in which the molecule of "fatal" nitrate is eliminated by filtration will therefore have few advocates, although the fertilisers produced by this means are relatively concentrated. This inconvenience could be minimised by specially treating the nitrate of lime so that it may be used in the manufacture of other fertilisers, but by doing so the capital outlay is higher.
2. Cost of transport - to quote an example, in countries where the costs of transport are relatively high, it is advisable to treat the phosphate by means of the phospho-nitric process rather than by the sulpho-nitric process; the former results in a much higher concentration, and the saving in transport costs justifies the installation of a phosphoric acid plant.
3. Price and availability of raw materials - The methods in which CO_2 is used are generally only economic if CO_2 is available gratuitously and fuel is cheap, as the slurries are comparatively diluted and the consumption of calories is therefore important.
4. Cost of installation - It is obvious that the available capital is a major factor in the choice of the process. The simpler the process, the less the capital outlay and the cost of production. Processes calling for one filtration or, worse still, several, lead to higher costs.

We are of opinion that the process of sulpho-nitric attack is one of the simplest; if, after having utilised such a plant for several years, the manufacturer wishes to produce more concentrated fertilisers, he need only instal a phosphoric acid manufacturing unit, and use the phosphoric acid instead of sulphuric acid. He can then manufacture a very great variety of fertilisers.

The Cie. de Saint-Gobain introduced several years ago these different processes and then retained those which seemed to them the best from an economic point of view, the only one that counts in the long run. They installed in their works units for the use of sulpho-nitric and phospho-nitric attack. Since then a certain amount of publicity has been given to the processes using CO_2 . The Cie. de Saint-Gobain examined this matter and decided that, in spite of the attraction which these processes seemed to have at the first glance, their future is not yet assured.

Comparison of the use of CO_2 with the use of sulphuric or nitric acid

We leave aside in our investigations the processes necessitating filtration or drying in order to eliminate a product or by-product, as we consider this operation as expensive, not only on account of the cost of the operation as such, but on account of the dilution of the slurries which it requires, a dilution which obviously results in a very costly final drying.

In the first place it must be emphasised that CO_2 can never be an agent for the solubilisation of phosphate as can nitric acid, sulphuric acid or phosphoric acid, which transform tricalcium phosphate into mono- or di-calcium phosphate, which is easily assimilable by plants.

On the other hand, CO_2 can fix the lime contained in the molecule of nitrate of lime which is to be eliminated, in the same way as can H_2SO_4 or H_3PO_4 , as indicated before. The role of CO_2 is thus confined to the elimination of this lime molecule, while the assimilable P_2O_5 , deriving from the nitric attack, can combine with the P_2O_5 , resulting from the utilisation of an excess H_2SO_4 or H_3PO_4 ; this latter constitutes by its presence, a further enrichment of assimilable P_2O_5 . Moreover, H_3PO_4 can combine with ammonia, thus forming ammonium phosphate, which enriches the content of the fertiliser not only in P_2O_5 , but also in ammoniacal nitrogen.

In these circumstances it is not surprising that the sulpho-nitric and phospho-nitric processes result in a very wide choice of $\text{N}/\text{P}_2\text{O}_5$ combinations, ranging from 1 to $1/3$ or $1/4$.

As, on the contrary, since CO_2 does not act as a solubilising agent of phosphate, it is necessary to introduce nitric acid in a strictly molecular proportion to the phosphate, which results, without any possibility of variation, in a combination $\text{N}/\text{P}_2\text{O}_5$.

It therefore follows that unless a partial acidulation of the phosphate and, consequently, an insufficient solubilisation thereof is assumed, an equilibrium $\text{N}/\text{P}_2\text{O}_5$ higher than, or equal to, 1 results, so long, of course, as there is no addition or extraction from the product while in the course of manufacture.

On the other hand, it is possible to obtain by means of phospho-nitric solubilisation, formulas of high concentration such as 14-14-14 or 12-15-18 owing to the fact that the phosphoric acid radical is itself a fertilising element, concentrations which cannot be achieved by using CO_2 .

From the foregoing it follows that, owing to the rigidity of the possible formulas and to their moderate concentration, a method employing the nitric attack together with CO_2 cannot be compared with the phospho-nitric or sulpho-phospho-nitric solubilisation.

In comparison with the sulpho-nitric methods the use of CO_2 , even if it results in concentrations which are very slightly superior (12-12-12 with a content of phosphate of 33.5% P_2O_5 and of chlorine of 60% K_2O , as compared with 11 1/2-11 1/2-11 1/2 or 12-11-12), lacks the elasticity which most manufacturers desire in order to enable them to offer their clients several formulas.

Let us now compare these methods from the point of view of economy.

In the sulpho-nitric methods the item H_2SO_4 of the cost price only represents about 5% thereof, and this is the maximum economy which can be effected by using CO_2 , even when this is available free of charge.

But the use of CO_2 entails:

- (a) a less favourable proportion of moisture, and therefore higher drying costs;
- (b) a more complicated apparatus, and consequently higher production costs;
- (c) higher losses in nitric and ammoniacal nitrogen.

It may be asserted that:

By comparison with well established sulpho-nitric processes, such as that used by Saint-Gobain, which requires only very simple apparatus and entails only small losses, the use of CO_2 , even if available free, has no advantage whatever.

It is different if a comparison is made with processes which are less perfect, particularly with those entailing a high loss of N.

SAINT-GOBAIN PROCESS:

The Saint-Gobain process employs the sulpho-nitric or phospho-nitric attack of phosphate.

In both cases the process and the apparatus are the same.

The process consists of the following stages:

attack of raw phosphate by a mixture of nitric acid and either sulphuric or phosphoric acid.

ammoniation of the slurry resulting from the attack,

addition of fines and ultimately of potassium salt to the ammoniated slurry,

granulation,

screening and crushing the granulated product.

The end product contains either equal proportions of nitric and ammoniacal nitrogen, in which case the phosphoric acid is present in the form of dicalcium phosphate; or it contains more ammoniacal nitrogen than nitric nitrogen, in which case the P_2O_5 is present in the form of ammonium phosphate and dicalcium phosphate.

By means of intensive study of the conditions of attack and ammoniation, Saint-Gobain have succeeded in evolving an extremely simple installation as regards number and construction of items of equipment.

This factor results in important economies of stainless steel and, consequently, reduces capital outlay and costs of manufacture.

Over and above the simplification of apparatus Saint-Gobain offer the following advantages:

1. Crushing of the raw phosphate is not necessary. This costly operation is obviated by a special design of the reaction vessel. The size of the raw phosphate particles is only limited by the usual apparatus for continuous weighing, which, obviously, cannot deal with particles which are too large.

2. A high yield of nitrogen: Saint-Gobain have reduced to the minimum the losses in nitric and ammoniacal nitrogen; actually the proportion of nitrogen delivered to the consumer compared with nitrogen used in the Saint-Gobain plant in the form of nitric acid and liquid ammonia has reached 98% a percentage calculated over a working period of two years in large industrial plants.

3. Great elasticity: the Saint-Gobain process permits the manufacture of products with a ratio of P_2O_5 (in the form of dicalcium phosphate) and nitrogen (half nitric and half ammoniacal) of 1.5 in the case of phospho-nitric treatment.

In addition, the same plant with the same apparatus can be used in both cases. Moreover, a corresponding quantity of soluble potash may be modified at request.

4. Not only is an economy made in sulphuric acid, but a saving of equal importance is effected in the manufacturing costs. The extremely simple plan and apparatus of the Saint-Gobain process make it possible to effect considerable economies in the use of power, maintenance and labour.

Further, the well-known advantages of compound granulated fertilisers must not be forgotten: economy in sulphuric acid, excellent keeping qualities of the fertiliser in stock, easy spreading owing to granulation, economy in bagging and transport as a result of high concentration.

It must also be emphasised that, contrary to certain adverse statements made, the fertiliser so produced does not involve any risk of fire or decomposition when stored. Saint-Gobain have never observed such deterioration in this type of fertiliser when stored.

The production of compound fertilisers is carried out by Saint-Gobain in their works at Rouen and Chauny, which have a total production capacity of 170,000 tons per annum.

The process is the following:

The nitric acid is utilised at a density of about 36° Bé, its flow is regulated by a calibrated orifice with a regular charge of acid; the sulphuric acid is at a concentration of 78% of H_2SO_4 (60° Bé) the phosphoric acid at 50% P_2O_5 ; the flow of these two acids is regulated by a bucket wheel of the ordinary type, but modified by Saint-Gobain, in order to improve its precision.

The material used is Morocco Phosphate (without grinding) which is fed by an improved belt poidometer.

Trials have been made with Gafsa and other phosphates; they have given the same results as Morocco phosphate. The attack is

made in chambers fitted with very effective agitators and means to avoid the generation of froth. The slurry obtained is ammoniated by anhydrous ammonia in chambers similar to the reaction vessels. The total volume of these chambers used for attack and ammoniation, necessary to produce 400 tons of fertiliser daily, is 20 m³. For such a plant the total requirements of stainless steel do not exceed 10 tons. Potassium chloride and the fines are introduced into the ammoniated slurry by mixers of small dimensions. Afterwards the product passes through a granulation drum and dryer. The granules are cooled and screened.

To give an example, we enumerate below some formulas which can be realised by means of the Saint-Gobain process. The consumption of raw materials per ton of fertiliser corresponds to industrial results.

11/11/11. 10/10/17. 12/15/18. 14/14/14. 10/20/20. 20/20/0.

Mor.Phos.(Kgs)	330	309	256	241	194	275
HNO ₃ (in the form of acid of 36°Bé (Kgs.))	255	232	274	315	184	432
H ₂ SO ₄ (in form of acid of 60°Bé (Kgs.))	117	107	-	-	-	-
P ₂ O ₅ (in form of acid of 50% P ₂ O ₅ (Kgs))	-	-	65	62.5	137	107
H ₃ N anhydrous (Kgs)	66	61.5	74	87.5	75	127
Potass. Chloride @ 60% K ₂ O (Kgs))	189	284	300	240	332	-
Energy (Kwh)	30	30	30	30	30	40
Fuel oil (Kg)	25	25	25	25	25	25

A unit of 200 tons per day requires about 7 men per apparatus. The building necessary to shelter it is 18m x 18 m x 18m; the maintenance costs in France amount to about 350 Frs. per ton.

Conclusion:

If in the choice of a process economy of sulphuric acid is important an economy in production is still more so.

A process which does not require sulphuric acid is interesting, but what is its value when considered from the point of view of investment, requirement of stainless steel, elasticity and maintenance?

The processes in which nitrate of lime is a by-product necessitate the sale of a certain quantity of this product or its incorporation in other fertilisers.

The processes involving the separation by filtering of certain products and the incorporation into a final product call, apart from complicated installations, for a great dilution of the slurry, and in consequence entail a large consumption of calories to dry the material.*

* The use of CO₂, even if gratuitous, either results in a small range of formulae or, if a separation of certain products is made in the course of manufacture, in expensive installations and, in both cases, the fuel consumption is high.

After studying all these processes, Saint-Gobain's choice has fallen on the processes using a sulpho- and phospho-nitric attack and they have perfected a technique which appears one of the most economical, even when compared with certain processes which have recently been advocated, but which, to our knowledge, have not yet passed the experimental stage.
