

ISMA* Technical Meetings

Cambridge, United Kingdom

15-17 September 1953

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

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LE 399
TECHNICAL MEETINGS 1953

September 1953

Paper ~~(b)~~ 3 ~~(c)~~ 2

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NOTES ON A PILOT-PLANT FOR THE MANUFACTURE OF PHOSPHORIC ACID BY THE WET PROCESS.

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INTRODUCTION: General observations.

Among the raw materials required for the production of fertilisers, phosphoric acid is daily gaining in importance. As a matter of fact consumers show an increasing interest in fertilisers. The phosphoric acid content of high-grade fertiliser and of superphosphate in particular, is limited to comparatively low values owing to the P_2O_5 content of phosphate rock. The richest of the latter does not enable the manufacturer to go beyond 18 or 19%. In order to go beyond this limit it is necessary to use phosphoric acid by means of which it is possible to obtain concentrated superphosphates.

The manufacture of phosphoric acid by the dry process has not in fact been generally adopted in European countries, especially in France, owing to the excessive price of electric power. Although the wet process constitutes, in fact, a waste of sulphuric acid seeing that the latter, of primary necessity, is converted to sulphate of lime, a bulky residue to be discarded, it is this process which is almost exclusively adopted by the manufacturers of phosphatic fertilisers.

In addition to the above mentioned disadvantage in connection with the wet process, there are two further drawbacks to be considered:

- 1) It produces a very impure acid containing iron salts, calcium salts, sulphuric acid and fluorine containing compounds; with the exception of special cases however, such as the manufacture of di-ammonium phosphate, these impurities do not constitute a great disadvantage for ordinary usages.
- 2) It provides only relatively diluted liquors which have to be concentrated by evaporation which, in addition to fuel costs give rise to problems of corrosion and furring, which are sometimes difficult to solve.

The studies which we have undertaken since 1937 have resulted in 1949 in the erection of a pilot-plant functioning since then at the

MONDEVILLE works, near Caen. This work was aimed at producing by the wet process, as concentrated a phosphoric acid as possible in order to permit its direct use, without evaporation, in the manufacture of concentrated superphosphate without the necessity of modifying the apparatus for the manufacture of ordinary superphosphate.

Preliminary studies.

At the time of which we are speaking, the known and applied processes produced in general phosphoric acid containing only 20 to 25% w/w P_2O_5 , sulphate of lime being invariably obtained in the form of gypsum.

Moreover, if this process has since then been developed to give a 30/32% acid, the methods by which sulphate of lime is precipitated, either in the form of semi-hydrate or anhydrite, have, to our knowledge, not yet been applied on an industrial scale, although they have formed the subject of some very interesting papers which have been presented here in France by S. NORDENGREN.

Experiments carried out from 1937 to 1943, at first in the laboratory and subsequently on a semi-industrial scale, have enabled us to work out a process based on gypsum which produces, from North African phosphates and 75% sulphuric acid, a phosphoric acid with a density of 1.40 containing about 32% of P_2O_5 . An adequate filtration speed is achieved by crystallisation of the sulphate of lime in a satisfactory form.

During this period filter materials have been studied and this problem was subsequently solved in a highly satisfactory manner by the use of textiles based on synthetic resins. The resistance of materials to the action of hot and impure acid has also been studied.

Events taking place in the year 1944, especially in our region, retarded the construction of an industrial plant until 1949. It would have been possible, at the time, to construct without delay an up-to-date works since research work, similar to ours, had been carried out on a small scale in various places and would have permitted at that time the installation of efficient plants having a steady output.

It was, however, considered preferable to commence by installing a pilot-plant with a small capacity and with a comparatively short period of operation, which would permit of the application of various variations of the wet process. This plant has, as a matter of fact, focussed attention on certain practical difficulties which appear on an industrial scale only. In addition, the value of the manufactured product, although the cost price was, of necessity, higher than in a plant with a large output, allowed an appreciable return for the cost of development and gave added justification to the installation of a pilot-plant.

In describing this small installation it is not our intention to represent it as a technical innovation. We were of the opinion, however, that it was of interest to demonstrate the principle of an experimental plant much favoured in the United States but less in evidence in Europe.

Technique of manufacture.

The process adopted is discontinuous and is characterised by a series of single and independent operations. This procedure obviously gives a smaller output than a continuous process but it simplifies the apparatus and, above all, it enables the manufacturer to

observe at once the effect of any variation in the operating conditions.

With a continuous apparatus, on the contrary, the mass of the products undergoing reaction is, of necessity, voluminous compared with the production per unit of time and the effect of any modification noticeable is only after a period which may be considerable.

In addition the chosen process allows intermittent or continuous operation in one, two or three operations a day, stoppages and restarting not presenting any special problem.

The technique which has been developed in the course of preliminary experiments with gypsum is as follows:-

The ground phosphate rock is attacked by phosphoric acid of a fairly high concentration, from previous operations, containing 25 to 28% P_2O_5 by weight and of density about 1.30.

If it is desired to work at a higher concentration, the quantity of this acid must be correspondingly higher. One is limited in this respect by the diagram for the state of hydration of calcium sulphate which has been established, especially by NORDENGREN. For a final concentration of 32%, corresponding to a density of 1.38, the temperature of 85° cannot be exceeded without risking the formation of semi-hydrate crystals which retard the filtration.

In any case, the diagrams in question have been established for pure acids and in the case of acids, containing salts in solution as well as sulphuric acid, with a P_2O_5 content considerably lower than that of a pure acid of the same density, the curves are slightly modified, or to be more exact, there may be a retardation in crystal transformations.

It is possible to carry out the attack at a slightly higher temperature without modifying the crystalline form especially if precipitation of calcium sulphate takes place at a temperature and concentration which corresponds to a point shown on the curve of separation of the zones gypsum/semi-hydrate. As a matter of fact, it is possible to assume that at the moment of introduction of sulphuric acid to the magma, the solubilisation of the P_2O_5 of the phosphate is not instantaneous but progressive. The concentration of the P_2O_5 therefore does not attain its maximum and a rise in the temperature at that moment has no disadvantage, but on the contrary, permits of a more rapid reaction and a more complete attack.

With a given initial concentration and temperature, the crystals size of calcium sulphate and consequently the speed of filtration and the facility of washing, depends in particular on the volume of recycled phosphoric acid, i.e. in short, on the quantity of water in the presence of which calcium sulphate is precipitated.

If 2,500 litres of phosphoric acid are recycled per ton of phosphate which corresponds (at a concentration of 26%) to approximately 1.5 times the quantity of P_2O_5 contained in the phosphate, large crystals are obtained which are readily filtered and washed.

The recycling of the sludge from a preceding operation in place of the filtered acid, a process particularly applied by DORR, does not seem to us advantageous as compared with our mode of operation.

In a batch process it is a question of time-saving in order to reduce the time of attack to a minimum retaining at the same time a satisfactory rate of extraction of P_2O_5 . For this reason and on account of the small dimensions of the apparatus which causes

increased heat losses and in addition owing to the comparatively low concentration of the sulphuric acid used, we have been induced to heat the vessel used for the attack in order to maintain the temperature at 85°. Under these conditions the complete time of attack did not exceed 1.15 hours.

The phosphate is introduced into the phosphoric acid raised to a temperature of 60° and submitted to vigorous agitation for approximately 15 minutes, after which sulphuric acid is added rapidly at room temperature. The temperature rises rapidly to 85/90° which is maintained by heating, and agitation is decreased at the same time in order to assist the formation of crystals. After an hour the magma is ready for filtering 98% of the P₂O₅ having been solubilised.

Filtration and washing are the subject of special arrangements which we propose to describe when dealing with the apparatus.

Description of apparatus.

The installation is characterised by two special features, the remainder being built on the usual lines.

- 1) Both filtration and washing is carried out in a continuous centrifugal drier with a horizontal axis and automatic extraction of the cake.
- 2) Washing is carried out with liquids the concentration of which is progressively and continuously decreasing thanks to an appropriate device.

The dimensions of the apparatus have been determined by the size of the drier. The largest model available at that time requires a tank (panier) two metres in diameter with a capacity of 1,100 litres. As each batch has to be filtered in one operation the quantity of the treated phosphate per batch may not exceed 400 kgs.

Choice of the combined drier and filter was the result of several considerations. Experiments on a semi-industrial scale were carried out with vacuum filters. In a discontinuous installation the output of such apparatus is fairly small; on the other hand continuous filters, e.g. band filters, are made for productions much higher than those to which we had agreed to limit ourselves. (2 to 3 tons of P₂O₅ per day.)

Experiments conducted with a small model of the drier with a tank of 0.50 metres, had shown that the speed of filtration could be highly satisfactory, that the washing was very regular and complete and that, due to thorough drying, the calcium sulphate extracted by the scraper was in the form of a powder which was hardly moist although it contained about 20% water. This indicates a potential use for the latter, especially after drying, as a filler in mixed fertilisers.

Another advantage of the drier is that the filtrates are discharged into the open which avoids all questions of joints, airtight receptacles and of extraction by pump or barometric column indispensable to vacuum filters.

Lay-out of plant. (See diagram attached)

The plant was housed in an existing concrete building arranged on a metal framework on the principle of gravitational flow.

At the top at a distance of 10.50 metres from the floor is a hopper for ground phosphate coming from the grinding plant; the

maximum fineness of Morocco phosphate (Kouribgha) corresponds to a residue of 10% on sieve No.150.

Below is an automatic weigher and a volumetric gauge for the sulphuric acid from a lead chamber plant (Gaillard system.) This acid with a density of 1.65 contained 75% of H_2SO_4 . On the same floor are tanks for the recycled phosphoric acid (provided with coils for re-heating and cooling,) tanks for weak washing acid and a water-heater for the final washing.

Further below is the only mixer in which mixing takes place successively and in an order which can be varied according to requirements. It is a "Dietrich" apparatus of 2,000 litres capacity, the hemi-spherical bottom of which is double-walled thereby permitting heating with steam at low pressure. The tank for breaking down the phosphate is of steel lined with lead. (plombe a la goutte?) The agitator with variable speed is of 18/8 stainless steel containing molybdenum. The paddles as well as the baffles fixed to the cover form an anti-froth device. The generated gases are drawn off through steel pipes lined with ebonite and carried to the washing installation of the superphosphate plant. The apparatus is emptied through the bottom, lead piping conveying the sludge to the drier placed on the lower floor.

The drier is a "Robatel" apparatus of the two-metre-type with a very large blade for scraping. With the exception of the shaft which is yacheted the drier is made completely of 18/8 stainless steel containing molybdenum. The tank has a diameter of 2 metres and a thickness of 0.80 metres which gives a filter surface of about 4.5 m². There is no lateral filter surface.

The vessel turns at 500 revs. a minute, the centrifugal force developed at the perimeter corresponding to 270 g. It is equipped with a 2 mm stainless steel gauze on which is placed the "Thermovyl" filter cloth. The latter is polyvinyl chloride (plasticised?) which can withstand a temperature of up to 90° without losing shape. The chemical resistance of this cloth is 100% and it lasts several months.

When fully charged the thickness of the cake in the vessel reaches 25 centimeters and the dried cake of sulphate of lime has a thickness of about 15 centimeters. This thickness, which is greater than when working with vacuum filters, indicates that the filtration is not as rapid as might be expected, taking into account the difference in pressure between the two types. This pressure has, however, the advantage of giving a regular and compact cake without the slightest fissure so that washing is completely uniform over the entire surface.

The removal of the dried cake is effected without stopping the vessel by means of a rabble arm in special "Uranus" steel operated by a hydraulic servo-motor; the removal of 650 to 700 kgs. of gypsum takes only 2 to 3 minutes, the disintegrated product forming a moist powder of a consistency similar to superphosphate.

The drier is mounted on springs on a concrete bed of 40 tons, which in turn rests on six pillars 2 metres in height by means of "Amortisseurs" and "Visco-freins" contrivances supplied by Ets. MONNET. Thanks to these devices, an accidental unbalance of the vessel caused for example, by an irregular charge, may produce oscillations of the machine of several millimeters' magnitude without causing any dangerous strain and without transmitting any vibration to the floor. All the tubing and the driving gear in connection with the drier have of course elastic joints. Once the machine is moving it consumes only about 15 horsepower units (C.V.) except at the moment of extraction additional load resulting from the breaking action of the rabble arm.

For washing, instead of following the usual procedure of successive washings with dilute acids, followed by water, the apparatus employed makes it possible to reduce the volume of the liquid required, by effecting the washing in one operation with a phosphoric acid solution the concentration of which decreases progressively to nil at the end of the operations.

This is based on the property of certain solutions of phosphoric acid of different concentrations being difficult to mix (it is known that one sometimes finds difficulty in obtaining a completely homogenous acid by mixing.) It has been observed that if the solutions enter a vessel slowly and at an appropriate point, no appreciable mixing takes place and thus it is possible to superimpose progressively diluted acids and to surmount them by a layer of water. Diffusion is very slow and does not take place in the course of manufacture.

A simple device in a deep tank renders it possible to classify the solutions by density. For the washing of the cake the solutions are taken from the bottom of the tank in the same order as they are fed into the tank.

As a matter of fact, in order to avoid stirring up the liquid when pumping it for the duration of the washing (especially with pumps without pressure valve where the over-flow is returned by suction) the weak solutions leaving the drier descend by gravity and classify themselves in a tank on the ground; a pump takes them up again in the same order and recycles them in a second identical classifying tank on top of the drier in which they will go through the following operation. During their passage they are reheated by a steam coil heat exchanger.

The liquid is kept moving by means of vertical Kestner pumps in stainless steel. The tubing is in lead or rubber.

The personnel comprises only two workmen one being at the mixer and the other at the drier. Control consists of continued measurements of temperature and density at different points of the circuit as well as of periodical titrations of P_2O_5 , SO_4 , etc. in the circulating solutions.

Results obtained.

Since this plant is purely experimental no endeavour has been made to attain an intensive production. However, periods of regular operations have made it possible to carry out a series of operations each of which lasted about 1.15 hours, both filtration and drying not exceeding 45 minutes. The drier would have been capable of dealing with a production of approximately 2.5 tons of P_2O_5 per 24 hours.

The filtration speed which varies a great deal according to the nature of the phosphate used, can, in the case of Morocco phosphate from Kouribgha, reach more than 100 kgs. of P_2O_5 per square metre of filter surface per hour.

Various qualities of phosphate have been used, especially Algerian phosphates from Kouif. In their natural state they require only coarse grinding and are readily attacked, but during attack they form a tenacious froth in voluminous quantities; after being calcined at low temperatures ($350/400^\circ C$) to destroy organic matter, this frothing is lessened but both the phosphoric acid and the gypsum assume a dark hue. After decarbonisation at $900^\circ C$, the phosphate no longer froths but requires finer grinding. Morocco phosphate, also requires fine grinding and produces little froth. The sulphate of lime always contains less than 1% of P_2O_5 on the dry weight and the extraction efficiency of P_2O_5 is round about 97%.

Corrosion resistance of materials.

For reaction at high temperatures at high sulphuric acid concentrations lead behaves best, but stainless steel even when containing molybdenum sometimes gives rapid corrosion, especially in the neighbourhood of welded joints.

18/8 stainless steel containing 3% molybdenum and rubber are fully resistant towards phosphoric acid at 80°C and above. Particularly for tubing rubber is preferable in view of the formation of scale by the alkaline fluo-silicate on cooling the acid. Owing to its pliability, rubber permits of easier cleaning than metal.

In this respect it should be noted that the fluo-silicate content of the acid is less if prepared at a higher temperature, owing to the greater volatilisation of fluorine-containing gases during the attack. For North African phosphates which contain little silica, volatilisation can be increased by adding to the mixture small quantities of precipitated silica.

Plastic materials and, in particular, polyvinyl chloride, (either hard or reinforced semi-pliable) constitute a material which is of great interest for tubing as the crystalline deposits do not adhere to the surface and can be removed simply by washing. In addition, they have complete chemical neutrality. Unfortunately these products soften considerably with rising temperature and are not pressure-resistant.

Plastic materials containing fluorine may perhaps be a definite solution of problems of corrosion when it is possible to fabricate them more readily and to reduce their price which, at present, is too high.

Conclusions.

The pilot-plant has served its purpose and the experience gained will make it possible to construct an industrial plant of normal dimensions in which it will be possible to apply a more up-to-date technique with greater chance of success.

U.F.E.P.C.

Schema d'une installation pilote pour la fabrication de l'acide phosphorique par voie humide

