

# ISMA\* Technical Conference

Brussels, Belgium  
10-13 September 1968

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

The Odde Process - Possibilities and Limitations.

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Introduction.

There is a growing tendency for farmers to apply phosphates to the soil in the form of complex fertilisers, i.e. fertilisers containing two or three of the primary plant nutrients N, P, and K (1). The reason for the increased acceptance of complex fertilisers is the farmer's desire to save time and reduce labour costs. When using single nutrient fertilisers, the farmer must either apply them separately, or mix them before use. Either method is time consuming and costly.

Concurrent with this trend there has in the last few years developed a world-wide sulphur shortage, which has resulted in significant increases in the price of sulphur. The prospects of this trend abating in the near future are rather dim (2). Sulphur is the cornerstone in the production of phosphatic fertilisers in a large part of the world, and the higher sulphur prices are therefore adversely affecting production costs.

For these reasons the fertiliser industry is increasingly looking towards non-sulphur-using processes - to complex fertilisers - to provide the necessary production capacity to meet demand in the years to come.

There are several possible ways of converting phosphate rock to a plant digestible form without using sulphur, directly or indirectly, but only a few have achieved commercial significance. Of these, the processes which base the acidulation of the phosphate rock on nitric acid (nitric phosphate processes) have been adopted to by far the greatest extent.

The nitric phosphate processes have been in existence for a long time. The first process in this category, which was developed into a commercially successful plant, was based on the inventions of Erling B. Johnson, Odde, Norway, from around 1930. The process, called the Odde process, gained rapid acceptance in Continental Europe, and in Norway. Several modifications of the process have been developed since that time, such as the Hoechst-Unde process, the Kampka process, the DSM-Stamicarbon process, and the Norsk Hydro process. Presently, these processes account for an annual production of about 5 million tons of fertiliser.

Recent studies (3) have shown the Odda process to be competitive even at the lower sulphur prices of several years back. The revolution in ammonia economics, caused by the introduction of the mammoth single train plants, has further enhanced the attractiveness of the Odda process.

The intention of this paper is to give a review of the Odda process as it is used by Norsk Hydro today, comment on limitations in the process and possible solutions, and discuss the possibilities of expanding the product line and using the process as a starting point for new products.

### Process Description.

In recent years, Norsk Hydro has been doing extensive development work to improve production techniques and product quality. The results of this effort were included in a new plant at Eidanger Works. The plant went on stream in the autumn of 1967. In the plant, 1500 tons per day of NPK fertilisers are produced in a single train. Design capacity was reached shortly after start-up.

Figure 1 provides a simplified flow diagram of the process. All the major features of the conventional Odda process have been retained.

Raw materials for the process are 58 - 60 % nitric acid, and phosphate rock. Most commonly used in the past has been the high grade Kola rock (85 % BPL) but, recently, lower grade African and North American rocks have been used. In general, all phosphate rocks may be used but, unless the rock diluent is silica or carbonates which can be removed in the process, the use of lower grade rocks will result in lower nutrient concentrations in the finished product.

The dissolution rate of the phosphate rock depends on the acid concentration, the degree of agitation, the residence time in the acidulation vessels, and the external surface of the rock particles. Particles up to about 10 mesh may be used, and more than 99 % of the phosphorus in the rock goes into solution. The acidulation vessels are stainless steel vessels equipped with agitators. Foaming is controlled by using vigorous agitation, which also speeds up the dissolution of the rock. Defoamers may also be used.

The acidulation is followed by separation of undissolved matter in a sand trap. The undissolved matter, mostly silica, may otherwise cause equipment erosion and product dilution. Some of the phosphate rocks contain very little acid-insoluble material, and in these cases the sand trap is bypassed.

The crystallisation and removal of the calcium nitrate tetrahydrate are the characteristic features of the Odda process. Norsk Hydro employs batch crystallisers which are operated sequentially, resulting in overall continuous operation (4). The crystals are large and of uniform size. The crystal suspension is filtered on a rotating vacuum filter with stainless steel cloth of 0.5 mm openings. The filter cake is washed with nitric acid, and the acid in the cake is subsequently replaced by water. The wash acid is returned to the acidulation step. The filters are designed and manufactured by Norsk Hydro to meet the particular requirements of the process.

The terminal crystallisation temperature determines the degree of calcium removal, which, in turn, determines the level of water-soluble  $P_2O_5$  in the finished product. The nutrient concentrations in the finished product and the water solubility increase with increasing degree of calcium removal. In the past, common practice was to cool to about 15 - 20 °C, which resulted in a product of 25 - 30 % water-soluble  $P_2O_5$ . Presently, Norsk Hydro's older plants are cooling to about 12 °C. The products contain about 50 % water-soluble  $P_2O_5$ .

Recent trends have been towards products of higher nutrient content and even higher water solubility. In the new plant it is possible to cool to about -5 °C with a resulting product of 80 - 85 % water solubility. About 1.4 million calories per metric ton P are removed in the crystallisers. In addition to the higher nutrient concentrations and higher water solubility, the removal of more calcium extends the range of thermally stable products (5).

The filtrate is neutralized in three steps by ammonia gas, and about half of the water is evaporated by the heat of neutralization. In the neutralization step the calcium present is precipitated as  $CaF_2$  and  $CaHPO_4$ , while the balance of the phosphorus stays in solution as ammonium phosphates with a molar ratio of N:P of about 1.3. Ammonium nitrate is also formed.

The N: $P_2O_5$  ratio of the neutralized liquor is about 1:1.7. This ratio may be increased to any level by addition of ammonium nitrate solution, if so desired.

The water content of the liquor is reduced to about 0.5 % in evaporators at reduced pressure. The concentrated liquor is prilled directly, or mixed with potassium chloride, potassium sulfate and other plant nutrients (Mg, B etc.) before prilling.

Prilling of NPK mixtures is a recent development. Norsk Hydro has for a period of three years operated a prilling tower with a capacity of 500 tons of NP or NPK formulations per day. The new plant includes a prilling tower where presently 1500 tons per day of NPK fertilisers are produced.

The advantages of prilling are: high capacity in one train; low recycle rates and hold-up in the process, which facilitate control of product composition and reduce over-dosage; no need for drying of the product; and low investment and maintenance cost. The prilled products are of uniform particle size, and have a pleasant appearance and excellent handling properties.

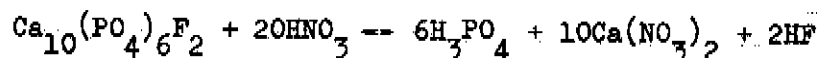
The prills are cooled and coated with a suitable conditioning agent prior to being sent to bulk storage and bagging.

The calcium nitrate tetrahydrate removed in the filtration is melted, neutralized, evaporated down to about 0.5 % H<sub>2</sub>O, and prilled to nitrate of lime fertiliser.

The Norsk Hydro process utilizes raw materials very efficiently. The recovery of P<sub>2</sub>O<sub>5</sub>, nitric acid, ammonia, and potassium chloride is in the 98 - 99<sup>2</sup>/<sub>5</sub>% range.

#### Product Concentration and Grade Flexibility.

The conditions in the acidulation and the degree of calcium removal in the crystallisation, determine the overall N:P<sub>2</sub>O<sub>5</sub> ratio of the process. It is necessary to maintain an acid to rock ratio that provides a small excess of acid based on the conversion:



The excess of acid is necessary to prevent precipitation of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> during the subsequent crystallisation.

For most phosphate rocks, the Ca:P<sub>2</sub>O<sub>5</sub> ratio is from 0.95 to 1.05. Based on the higher ratio and removal of the sufficient calcium to obtain 85 % water solubility in the finished product, the minimum N:P<sub>2</sub>O<sub>5</sub> ratio is 1:1.7. The absolute concentration levels in the products depend somewhat on the impurities in the phosphate rock used in the process. For most rocks with a P<sub>2</sub>O<sub>5</sub> content above 33 % and silica and carbonates as major impurities, the concentrations in the 1:1.7 product would come to about 18:31.

The process permits formulation of any  $N:P_2O_5$  ratio in the product above the minimum, and the inclusion of potassium salts and other plant nutrients. Examples of possible formulations and absolute concentration levels are 20:30:0, 23:23:0, 17:17:17, 23:11:11, 15:15:23, 13:20:20 and 13:13:26. These formulations are based on addition of potassium chloride.

If all the calcium nitrate removed in the filtration step is converted to ammonium nitrate and returned to the process, the resulting  $N:P_2O_5$  ratio would come to 2:1.

If all the calcium nitrate is processed to nitrate of lime fertiliser, the overall  $N:P_2O_5$  ratio of the process is 1.3:1.

#### Byproduct Utilization.

Presently, Norsk Hydro is marketing the byproduct calcium nitrate as prilled nitrate of lime fertiliser containing 15.5 % N. A diagram of the process is shown in Figure 2. Norsk Hydro's production of this fertiliser is close to 1 million tons per year with most of the raw material coming from acidulation of limestone. Nitrate of lime is well suited as a nitrogen source, especially for top dressing.

The nitrate of lime fertiliser is hygroscopic, but in closed bulk storage or in bags it may be stored for years without caking. Conditioning agents are not normally used. If desired, the hygroscopicity can be significantly reduced by coating with mineral oil.

An NPK formulation with 85 % water solubility would result in 4.4 tons of nitrate of lime fertiliser per ton of  $P_2O_5$  based on a  $Ca:P_2O_5$  ratio of 1.05 in the phosphate rock.

The production of nitrate of lime fertiliser is a convenient way of utilizing byproduct N. However, the calcium nitrate tetrahydrate may also be converted to ammonium nitrate.

The conversion of calcium nitrate to ammonium nitrate and calcium carbonate is a well known process. Norsk Hydro has developed its own version (Figure 3). The principal advantage of the Norsk Hydro process is that the absorption of ammonia and carbon dioxide and the formation of calcium carbonate take place in separate equipment. Thus, there is no formation of scale in the absorption column due to crystal growth. The ammonium nitrate may either be returned to the NPK process, or used to make ammonium nitrate prills with 33 % N, or used in other nitrogen-containing fertilisers such as ammonium nitrate limestone, etc.

### Product Properties.

It is known that mixed fertilisers containing ammonium nitrate and potassium chloride in certain ratios will undergo a self-sustaining decomposition when heated above the initiation temperature of 150 - 230 °C. This, however, is true regardless of the process used to manufacture the products. In recent years, much effort has been put into mapping the composition regions of thermal instability (5, 6). Today, it is possible to formulate stable products. Interestingly, the removal of additional calcium has expanded the range of compositions which are thermally stable (5).

The caking tendency of the products is overcome by applying a small amount of conditioning agent to the finished product. In bags, the storage properties are very good. With the new plastic bags available today, the conditioning may eventually prove unnecessary. Experiments being conducted now offer promise that bulk storage may be feasible.

Generally speaking, some precautions are necessary when handling NPK products, whether the products are made by the Odde process or by other processes. These precautions do not in any way limit the use of NPK fertilisers, and the additional costs are negligible.

### Process Economics.

Lately, studies of the comparative cost of producing complex fertilisers by the various processes available have been made (3). These studies clearly show that the mill cost per unit plant nutrient is lowest for the Odde process. This cost advantage is not only valid at present day sulphur prices, but also holds for the sulphur prices of several years ago. The plant investment for the modern Odde process will, in our opinion, be comparable to that of a plant based on sulphuric acidulation of the rock phosphate when the sulphuric acid manufacture is included. A turn-key price for a plant to produce 600,000 metric tons per year of prilled NPK 17:17:17 with 85 % water-soluble  $P_2O_5$  by the Norsk Hydro process is estimated to be about \$ 10 mill.<sup>2.5</sup> This figure covers the battery limit investment, and includes the calcium nitrate conversion plant.

The lower concentrations of the Odde products compared with the products from sulphur based processes influence the cost to the farmer (transportation, application). In the past the 1:1:0 product of the Odde process was 20:20:0. Today, when the concentration of the Odde product has been increased to 23:23:0, the difference in transportation and application cost has become of lesser importance.

### Agricultural Considerations.

Agricultural experiments have shown that the effect of nitric phosphates increases with increasing water solubility up to about 50 %. Tests over several years have shown that for most crops nitric phosphates with about 50 % water-solubility have the same fertilising effect as fertilisers with higher water-solubility. Some crops do, however, require a higher proportion of water-soluble  $P_2O_5$ . The modern version of the Odda process with products of about 85 % water-soluble phosphorus is able to meet this requirement and must be considered a highly efficient fertiliser for all crops.

### Future Prospects.

In the foregoing we have tried to establish "the state of the art" of the Odda process as it is practiced by Norsk Hydro today. It is evident that the process, regardless of the sulphur price, represents a most economical way of converting phosphate rock to a plant digestible form. The modern process also yields a product, which, from an agricultural point of view, is fully satisfactory for all crops. The higher concentrations of the product brings it more closely in line with the products from sulphur-based processes, which is important at a time when plants are becoming larger and larger and distribution costs attaining greater importance.

The present trend towards increased use of complex fertilisers, and the rapid increase in fertiliser production capacity, are expected to continue. Sulphur prices are expected to continue to climb, at least for the next few years. Against this background we expect that the Odda process will attain even greater importance in the future.

Yet the possibilities of the Odda process are far from being exhausted. It is interesting to read a paper presented to the Norwegian Engineering Society by Erling B. Johnson in 1930. Johnson discusses at length the possible applications of his inventions in the future. Today, one is struck by the foresight shown by Johnson. He talks about products of high water solubility and production of phosphates and ammonium nitrate. Many of the new developments in the Odda process fall within the scope of his thinking 38 years ago.

There is still ample room for further process improvements. The nutrient concentrations in the products could be further increased, and the minimum  $N:P_2O_5$  ratio lowered to increase grade flexibility. Other intriguing possibilities are using the Odda process as a first step in the production of:



NPK fertilizers and ammonium phosphates;  
industrial phosphates;  
phosphoric acid;  
polyphosphates etc.

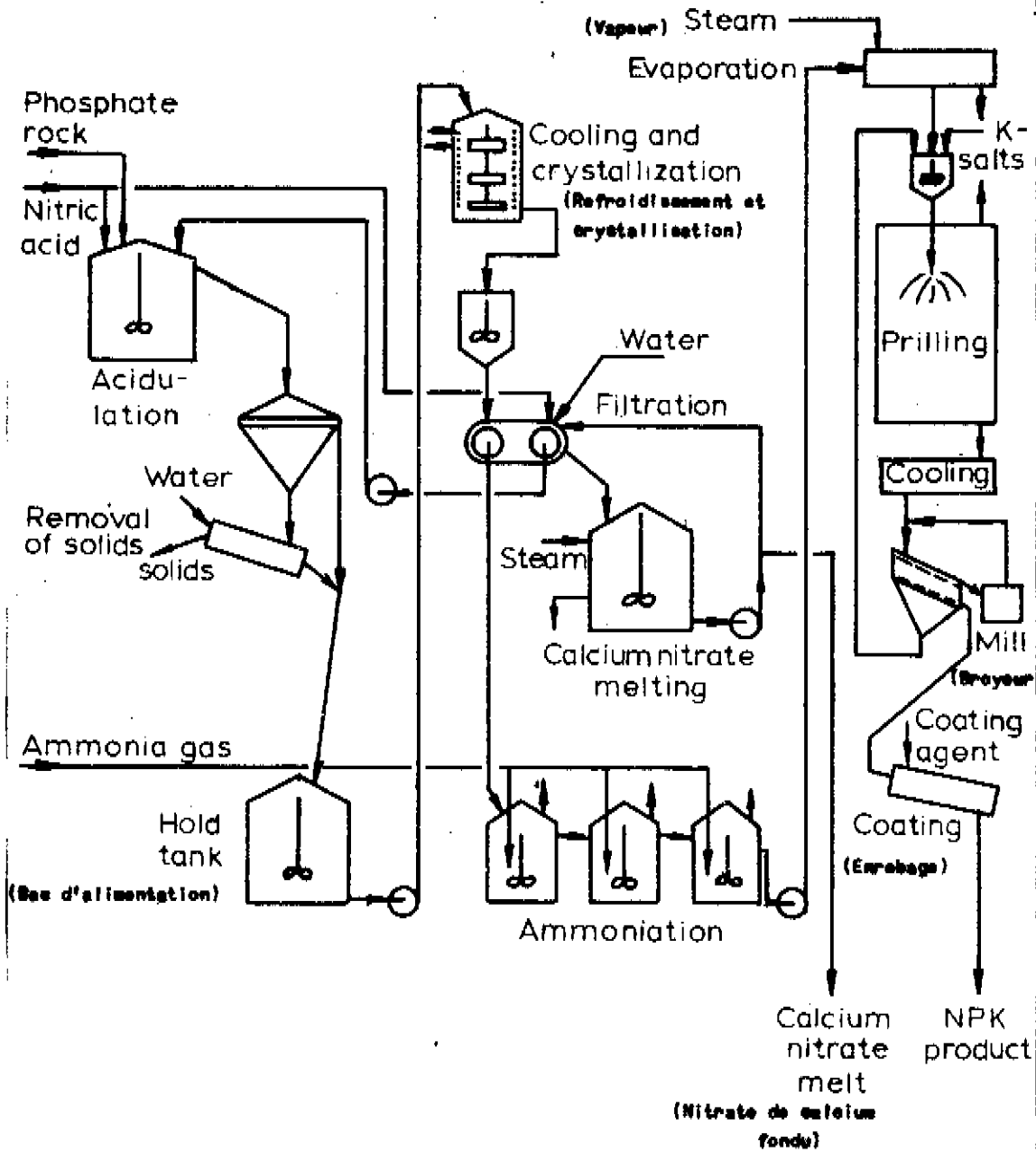
Some work has been done in these areas in the past but, today, more people are engaged in exploring these possibilities, as evidenced by the proliferation of patents and the articles being published. A survey of recent developments is given in (7). As interest in the Odda process continues to grow, and the resourcefulness of the industry is fully brought to bear on the problems, major steps forward are expected.

In conclusion, we feel that the Odda process is at last coming of age, and the possibilities, as envisaged by the inventor, are finally beginning to be put into practice. There is still work to be done fully to realise the possibilities of the process but, with the increased activity in this area, we expect new process modifications to emerge. Interest in the Odda process has been accelerated by the sulphur shortage, but, regardless of the sulphur situation, we think the Odda process will be able to compete in the future.

References

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FIGURE 1 THE NORSK HYDRO NPK PROCESS  
PROCEDE NPK DE NORSK HYDRO



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FIGURE 2

PRODUCTION OF NITRATE OF LIME

PRODUCTION DE NITRATE DE CHAUX

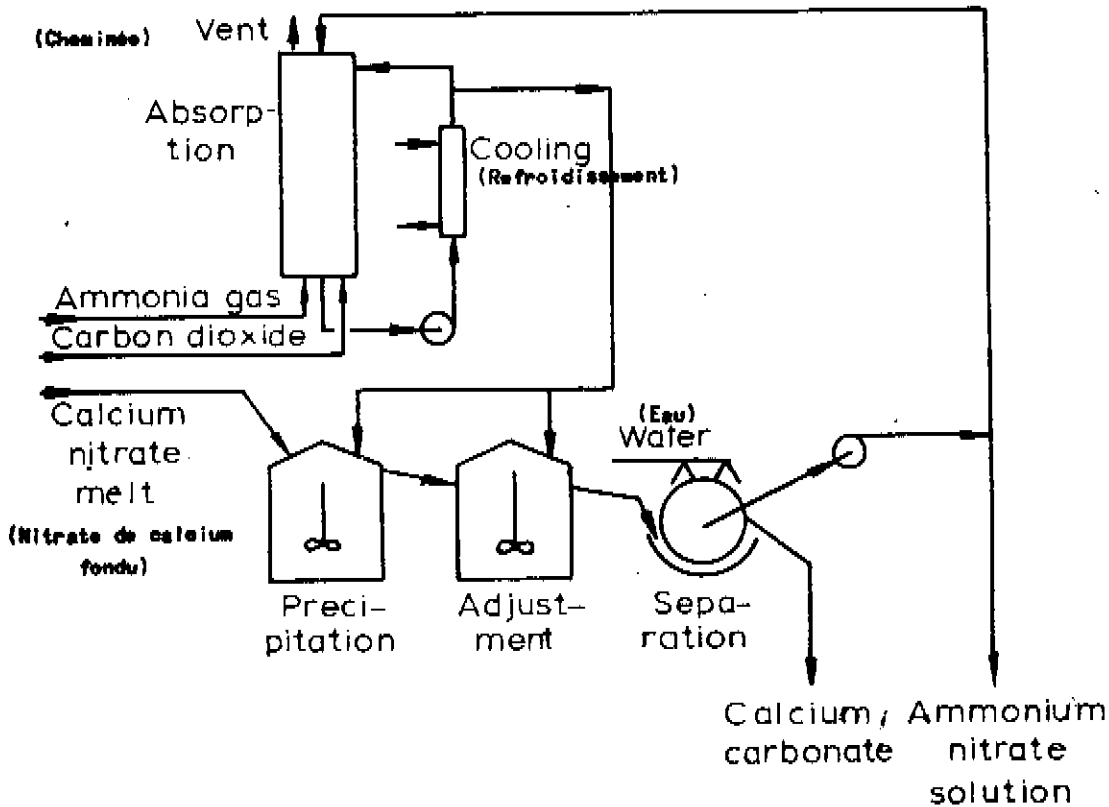
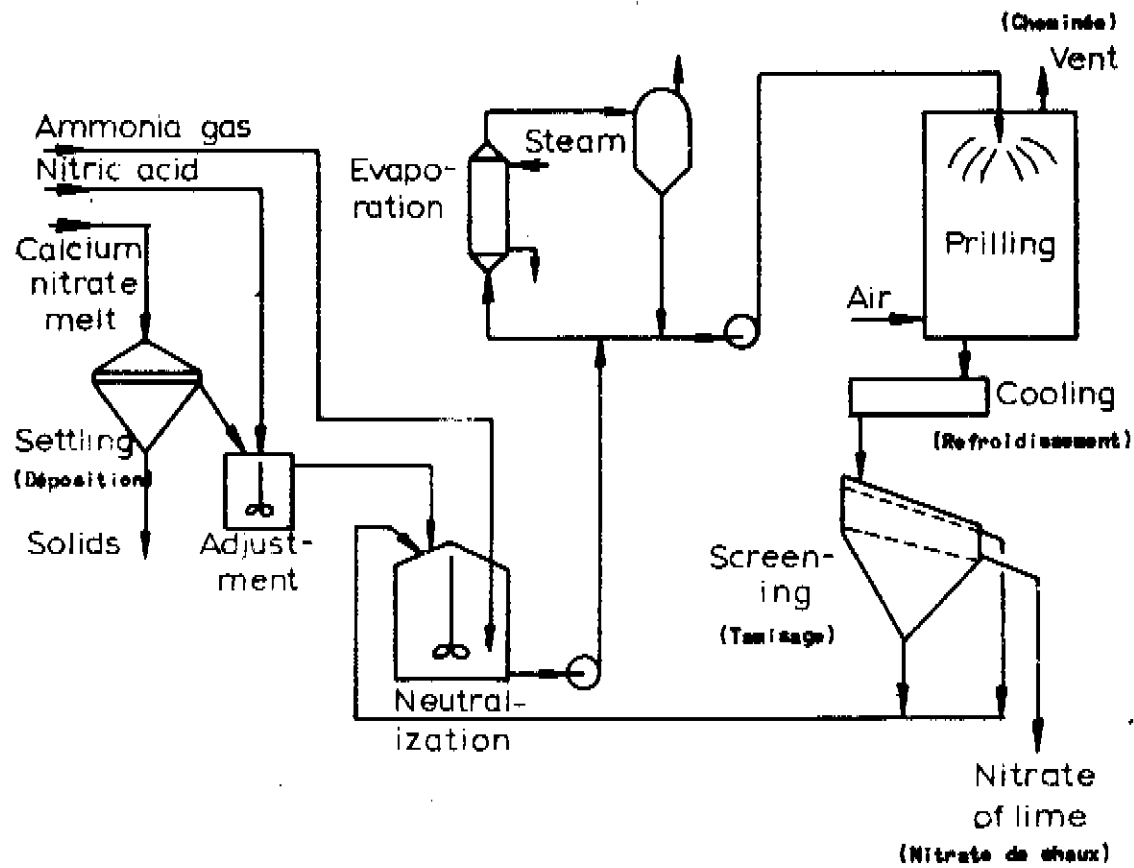


FIGURE 3

CALCIUM NITRATE CONVERSION

CONVERSION DU NITRATE DE CALCIUM

DISCUSSION

MR. O.H. LIE (Norsk Hydro, Norway): Let me start by making a correction in the text. In both the English and French versions on page 3, paragraph 3, it should read 1.4 million Kcal. rather than, as indicated, calories.

In my paper I try to give an impression of how Norsk Hydro is using the Odde process today. The process itself, of course, is comparatively old, and the process principles are common knowledge. Thus one might think that the possibilities of improving the process would have been exhausted many years ago. Yet as has been experienced in many areas of the chemical industry in recent years the application of new engineering techniques coupled with a critical analysis and extensive research of the important process steps of established processes can be very fruitful. In this respect the Odde process is no exception. The new Norsk Hydro version of the Odde process which is used today in a 1500 t/day NPK plant in Norway has a simplified process scheme compared to earlier Odde plants and yields products of improved properties. The nutrient concentrations in the product are higher, the water solubility of the P<sub>2</sub>O<sub>5</sub> is in the 80-85% range. The grade flexibility has been increased. Formulations of N : P<sub>2</sub>O<sub>5</sub> ratios of 1 : 1.7 can now be made. In addition, most formulations can now be made firmly stable even with the use of KCl, i.e. self-sustaining decomposition does not occur if they are ignited.

With respect to its competitive position it appears that history is on the side of the Odde process. Sulphur has increased in price while nitric acid is getting cheaper. Yet an economic comparison shows that, although the Odde process benefits from higher sulphur prices, it is competitive at sulphur prices considerably lower than those we have today. The limitation of the Odde process is still the restriction on the lower side in N : P<sub>2</sub>O<sub>5</sub> ratios and the need for marketing by-product calcium nitrate or ammonium nitrate if the N : P<sub>2</sub>O<sub>5</sub> ratio in the NPK fertilisers is less than 2. This is no serious problem in Europe, but in some other parts of the World it may be of greater importance.

In my paper I have briefly discussed possible uses of the Odde process for new products. From the reactions and the questions I got before the presentation today it is now clear to me that I should not have done this. For obvious reasons, I am not in a position to go into details on these questions, but it seems to me that the filtration liquor can be used as a raw material for the products I have indicated. Another question is whether these products should actually be made, and if they can be made economically. Only the future will tell about this. Looking back, it seems as if it has always been possible within the framework of the Odde process, as originally pointed out by the inventor Mr. Johnson, to meet demands imposed by changing market conditions. I am confident that this will also be possible in the future.

MR. Y. BERQUIN (Azote et Produits Chimiques, France): It is a great pleasure for me to open the discussion of this most interesting paper by Mr. Lie, since this gives me the opportunity to pay tribute to the precursors of the complex fertiliser industry. Indeed, although the very first patents for processes involving calcium nitrate filtration were taken out by the Odde Smeltewerke in October 1928, Norsk Hydro followed very close behind with its patents on the separation of the nitrate as double salts. And since this time, Norsk Hydro has continually brought to the fertiliser industry the fruits of its

experience in this field. This process is of great topical interest in view of the situation in the sulphur market in recent years. This is why I should like to ask the author certain questions:-

- 1) The paper indicates a provisional investment cost for a plant of 600,000 tpa of 17-17-17. To obtain a more complete estimate of the cost of this fertiliser, we should like to know details of the utilities consumption (electricity, fuel, steam, water) and if possible, the division between the two sections: complex fertilisers proper, and calcium nitrate conversion.
- 2) The process comprises a discontinuous operation, i.e. the crystallisation of calcium nitrate. Even the use of several tanks in parallel does not achieve the regularity of a truly continuous operation working in constant conditions. Does Norsk Hydro envisage any modification in this sense in the future? In particular, has the company envisaged using the recent process by which cooling is achieved by the infusion of an immiscible cooling liquid into the liquid to be cooled? If so, what conclusions have been drawn?
- 3) Would not the adoption of a continuous centrifuge be preferable to a rotating filter?
- 4) Is the process applicable to all phosphates, at least to those entering world trade, and must they be pre-treated in some special way, such as, for example, by calcination?
- 5) It is generally accepted that when the temperature of the crystalline slurry descends below 0°C the viscosity of the liquor greatly increases and gives rise to very fine crystals. The viscosity of the medium and the fineness of the crystals together considerably increase the difficulties in separating the calcium nitrate. Has Norsk Hydro encountered this difficulty, and how has it been overcome?
- 6) 85% water solubility implies the presence of a certain amount of dicalcium phosphate in addition to other solids in suspension in the slurry, such as insoluble iron and aluminium phosphates from the phosphate rock, etc. Does this general range of solid materials not cause any difficulty, particularly in the evaporator?
- 7) With regard to the previous question, we have learnt from other papers presented during this conference that certain companies prefer the classical drying process with a rotating dryer. In contrast, Norsk Hydro has chosen preconcentration followed by prilling. Can these different opinions be explained?

Finally, in a general way, I should like to raise the problem of high analysis fertilisers. This implies the increasingly complete absence of mineral elements which are nevertheless necessary for plant life. I am thinking in particular of sulphur which used to exist to a greater or lesser extent in practically all forms of unconcentrated fertilisers, but there are also other metals or metalloids which are equally indispensable and which were carried by these fertilisers. Is there not an agronomic limitation to the use of these highly concentrated and, therefore, very pure fertilisers?

MR. O.H. LIE: I should like to thank Mr. Berquin for his kind remarks.

With regard to utility numbers for this 600,000 t/year plant we have, I must admit, been deliberately vague on these points, since these particular figures would vary greatly according to local conditions. We have developed a set of approximate figures which we feel are reasonably applicable. The figures I am going to give you are per ton product produced: Steam 0.9 t, 25m<sup>3</sup> cooling and scrubbing water, 65KWH and 6 m<sup>3</sup> instrument air.

I cannot give you the breakdown of the cost between the NPK plant and the nitrate conversion plant. However the nitrate conversion plant is a low utility user, as I think is evident from the flowsheet at the back of my paper. Most of the energy consumed in that particular process comes in concentrating the ammonium nitrate liquor, and the amount used then depends on the amount of ammonium nitrate liquor returned to the NPK process. All the utilities in the nitrate conversion are a minute amount of cooling water and a negligible amount of electricity.

As for the second question I cannot share the view of Mr. Berquin on the question of obtaining continuous operation from a set of batch crystallisers. I think this is entirely possible. Other methods may have their merits, in particular in the use of direct cooling by an immiscible organic liquid. As I am sure you realize these are questions which my Company has been and is still looking at. But for the particular conditions in our process we feel that our present arrangement serves us the best. I think this will be clear in the answers to some of the other questions too.

Question 3 was concerned with why we don't use a continuous centrifuge. Continuous centrifuges are used by many of the Odda process users and, as far as I know, they have good experience with them. In our particular case we feel that our tandem filter which has its years of accumulated knowhow, is very well suited for the particular conditions we have in the deep cold crystal slurry from the crystallisers.

The fourth question related to the way we can use all the commercial phosphates in our process. As far as the chemical composition of these phosphates is concerned, I think they all yield very satisfactory products in our process. The level of some of the impurities, such as iron, aluminium and sulphur, should be kept at low values to minimise nitrogen losses in the acidulation step, if some of the components are oxidised there, and to obtain as high water solubilities as possible. Some of these elements may bind phosphorus in a non-water soluble form, thus lowering water solubility. Acid insolubles and large content of carbonates pose some operational difficulties. These problems, we feel, can be overcome by using vigorous agitation in the acidulation step and by the use of an efficient solids separation system. We are presently getting valuable experience by operating these types of rocks in our plants. Some do create problems admittedly, but I am confident that these can be overcome as we gain more experience. As for pre-treatment of the rocks, such as calcination, this may ease problems of operation. Ultimately, however, one has to decide which is cheaper: operating normal phosphates or using a pre-calcinated but more expensive rock. I don't think I have the answer today.

Question 5: you quite rightly point out the difficulties encountered when handling the crystal slurry from a sub-freezing, sub-zero, temperature and I think that these problems come back to the particular design of our crystallisers. With the batch crystalliser you are in an ideal position to be able to get large crystals under very controlled conditions, and the crystal size distribution is fairly narrow. In our particular filter cloth openings are also large, permitting some of the fine crystals from this very viscous slurry to go through and thus not to plug the filter. The result is a small loss in energy and water solubility, but the filtration process is greatly simplified and the loss of P2O5 in the filter cake is negligible by using this particular procedure. I think these two things more or less answer why we are using this non-conventional crystalliser filtration system.

6th question: the solid materials in our neutrilized liquor are not causing us very serious scaling problems in the evaporation step. Of course, some of the natural insolubles in the phosphate rock are removed before the evaporation. This step has worked much better in actual plant operation than we had expected in advance. Restoration of cooling or heating surfaces by flushing of the evaporator needs only to be done at very infrequent intervals.

Question 7 related to prilling compared to granulation and drying in a rotary dryer. I think this is a straight question of economics and technical knowhow. My Company has developed the prilling process which we think is very competitive. This is evidenced by the installation of prilling towers in some of our older plants. I cannot give you any comparative economic data here. I would just say that it has shown that prilling is a very efficient procedure. I also think that some of the operational advantages that I have indicated in my paper and the lowering of the hold-up time of the solid part of the process certainly simplify process control by cutting down the time constants of the system. Evaporation and prilling also eliminate these problems of a conventional drying process.

As for your last question, I think this is really a matter of philosophy, and I am not sure that I am capable of giving you the proper answers. I can only answer on the background of the Odde process by saying that most of these secondary or trace elements present in the phosphate are still in the final product. What has been removed is silica, and I don't think that is particularly useful, and calcium and, of course, the degree of calcium removal is a free variable in the process. As for the need for sulphur on the fields, without claiming to be an expert on this it seems to me that in this stage of increasing air pollution this need must at least be considerably less than in earlier years.

MR. P. MORAILLON (Pechiney St-Gobain, France): The finished product contains P2O5 in the form of dicalcium phosphate and ammonium phosphate, and the stated N/P ratio is 1/3, i.e. there is a large proportion of ammonium phosphate. Consequently, the fertiliser has a high pH, and one might therefore fear the formation of hydroxy apatite. This hydroxy apatite is soluble in neutral citrate but probably not in Joulie citrate which is the French standard. Could Mr. Lie state what is the respective solubility of the finished fertiliser in neutral citrate and in ammoniacal Joulie citrate?

MR. O.H. LIE: This question relates to the solubility of P2O5 in neutral and alkaline citrate solutions. As far as I know for both those 2 cases the citrate solubility is in the range of 98 to 100%. I must add a point on this: the Odde process, as more and more calcium is removed, becomes less and less sensitive to the formation of apatite in the product.

MR. GLIKIN (Simon Carves, U.K.): Have the authors considered the economics of nitrophosphate processes where ammonia is not manufactured on site but is imported?

With the increasing trend towards shipping ammonia and the possibility of further reduction in the cost of ammonia it would appear that a nitrophosphate process which requires CO2 may not be so attractive compared to the fertiliser process using phosphoric acid, nitric acid and ammonia.



MR. O.H. LIE: It seems to me that it is clear to everybody that the price of the final product must be strongly related to the price of ammonia. I think it's rather evident that fertiliser manufacturers would get a position in this particular raw material considering its great influence on potential profit. The position of the Odda process when you don't have any CO<sub>2</sub> is that you do have a by-product calcium nitrate, and if this is your particular position I certainly hope that you are able to sell it. There is the possibility that you can do things with calcium nitrate which are not done today and where you do not necessarily have to go to ammonium nitrate. But I think that these things belong to the future and as an answer to your question I think what I said is probably true.

MR. S. STRELZOFF (Chemical Construction Company, U.S.A.): How often do the filters used for the separation of calcium nitrate crystals need to be shut down to clear the filter cloth, and what is the life time of the filter cloth?

MR. O.H. LIE: With regard to plugging of the filter, as I indicated in some of my previous answers, the filter cloth openings are of such a magnitude that we don't get any plugging, so this is not a serious problem. As far as the life time of the filter is concerned, this I cannot tell you. I have, at least, a feeling that it takes a very long time before they wear out. This is due to the fact that they are made of stainless steel. They rotate at a rather sedate speed and there is really no wear and tear.

MR. S. STRELZOFF: What type of filters are you using?

MR. O.H. LIE: As far as I know we are using our own make. It's a stainless steel horizontal cloth.

MR. S. STRELZOFF: When using high grade phosphate you obtain a finished product with 80-85% water solubility by cooling down to -50°C. If you had to use good quality Florida phosphate, would you be willing to guarantee the same results?

MR. O.H. LIE: Yes.

MR. S. STRELZOFF: What are the limitations as far as the quality of rock phosphate is concerned? There are processes which claim they can use any grade of phosphate: Are there any low grade phosphates you would not accept?

MR. O.H. LIE: There are certain elements such as iron and aluminium which, if they are present in large quantities, might reduce water soluble P, and thus I would say that they are undesirable. To me it seems that it is a question of quality and prices and, if the price is right, you might use phosphate of low quality.

MR. S. STRELZOFF: What change is needed in your process to obtain 95 to 98% water solubility?

MR. O.H. LIE: That is, of course, a very loaded question. I would say that you can obtain 100% water solubility by removing from the neutralized liquor and filtrate the calcium or dicalcium phosphate, and you would essentially get a liquor containing ammonium phosphates and ammonium nitrate.

MR. S. STRELZOFF: Have you tried to do that?

MR. O.H. LIE: Yes.

MR. S. STRELZOFF: Did you obtain very easy filtration?

MR. O.H. LIE: Well, it can be done, and I think we do have some patents on that.

MR. S. STRELZOFF: In case of water solubility exceeding 50%, do you have any apprehension about stability for the use of your product for NPK mixtures?

MR. O.H. LIE: I don't think I should preempt the next speaker by answering that question. I think the question of water solubility, and its effect on product stability was very well elucidated by Mr. Steen of Norsk Hydro in Stresa last year. And the only thing I can say is that by removing more calcium you also expand the range of possible product compositions which are firmly stable.

MR. S. STRELZOFF: What is the retention time for mixing NP and potash?

MR. O.H. LIE: It's very short - a matter of seconds.

MR. S. STRELZOFF: Does your price of \$10 million for 600,000 t/year for real NPK include conversion of calcium nitrate, rock handling and finished product handling?

MR. O.H. LIE: It does include the cost of the nitrate conversion.

MR. S. STRELZOFF: I do agree with your statements that there is still room for further improvement of your process. As far as the sulphur shortage is concerned, it could be very temporary, and there are already some signs, in the U.S. at least, that the price of sulphur is going down. Do you think that the nitrophosphate process has any future in the U.S.?

MR. O.H. LIE: Yes, I think so. I refer to the TVA publication in my paper, and anybody interested might read that. I think that the particular comparison is based on a sulphur price of about \$32 per short ton, and the present price is considerably higher than that in spite of the slight decline you refer to.

MR. G. LUTH (B.A.S.F., Germany): I should be interested to hear what temperatures you use to prill the product. As is well known, mixtures of nitrate and chloride must be fairly carefully handled, because they can decompose. If you prill melts with only 0.5% water, you need very high temperatures. How high are these temperatures, and how do you solve the problem of security?

MR. O.H. LIE: The particulars of the prilling process are really company knowhow but I can say that prilling occurs between 150-180°C. As far as the stability of the product from prilling is concerned, we have of course now prilled for seven years in one of our older plants where we have produced 400 t/day, and in the last year we have had a 1500 t/day plant in operation, and I can assure you that the products are perfectly stable. There is no problem in that respect.

MR. G. LUTH: My question did not so much concern the stability of the product as the stability of the melt before prilling. Do you not fear an explosion?

MR. O.H. LIE: With regard to the stability of the melt prior to prilling, the only problem you have there is a slight loss of ammonia but, as far as safety precautions are concerned, as far as I know I don't think it is a serious problem. Of course we do have a very low content of  $\text{CaHPO}_4$  which might be of some importance here, and at the time you mix the chloride your temperature would go down very quickly, so this is a very short interval.

MR. R. DURAND (Kaltenbach & Cie. France): Could Mr. Lie give us the granulometry of the separated crystals of calcium nitrate?

Secondly, with regard to the control of the ammoniation in the three stages of the Norsk Hydro process, what are the methods used not only for laboratory control but, particularly, for automatic control?

Thirdly, with regard to the limits of prilling with mixtures rich in P205 and K2O we know that prilling is a method which works very well when the viscosities of the solutions are relatively weak. But the higher the content of P205 and K2O, the higher the viscosities, which in certain cases can reach 10,000 centipoises, which makes prilling impossible. I should therefore like to know the limits of these P205 and K2O contents.

MR. O.H. LIE: You are asking a very intimate question here. I will try to answer as precisely as I can. Of course, there is a limit with regard to the ratio of the K2O to the melt from the vaporisers that you can tolerate. I think, however, that for most common compositions or formulations as indicated in my paper you have no serious prilling problems. But there is, of course, an upper limit where you add so much solid to your melt that it becomes too viscous to handle. I am afraid I cannot give you the limit on that.

Your second question relates to the control of the ammoniation steps in the process. There you have regular pH controls on your reaction tanks. pH control is a difficult thing in the process, due to the consistency of the liquor. However, we are using a system which seems to function rather efficiently on an automated basis. The retention time in the tanks, however, is of such magnitude that it is possible to operate rather safely without any sophisticated control equipment. With regard to the granular size of the calcium nitrate, I don't think I can give you the exact numbers on this but obviously they must be larger than 0.5 mm, otherwise they would have ended up in the liquor. I suspect that the size may vary slightly from one phosphate to another, but it is fairly large, and I think that the narrowness of the crystal size spectrum gives you a very open filter cake which makes handling of the cake very simple and reduces your P205 losses.

DR. B. RAISTRICK (Albright & Wilson (ACC Division), United Kingdom): Could you tell us at what point you return your off-size NPK to your prilling tower and what kind of problems you encounter in the way of decomposition?

MR. O.H. LIE: You are talking about the recycle in the prilling process, I think. The recycle feature of the prilling process is one of the most attractive things. I think you have most of the particles in the range of 1 to 4 mm, about 95% of them, and, depending then on the decided particle size distribution, I think you would return 5 to 10-15% back to your process. We do have some prilling parameters, of course, which allow you to vary the particle size distribution.

MR. B. BANDYOPADHYAY (Gujerat State Fert., India): I wanted to know about the prilling operation of NPK as stated on page 4 of the paper. What is the height of your prilling tower? Is there any fluidiser at the bottom of the tower, and is there any fluorine recovery system? What effect has the fluorine recovery on the prilling? What is the size of the prills? What is the strength? What percentage of losses are attributable to prilling tower dust?

MR. O.H. LIE: The size of the prilling tower is a function of the capacity of your plant. I think for a plant producing around 1500 t/year your prilling tower would be about 40 m high and 20 m wide. Dust losses in prilling processes are very low. The rising velocity of the air moving up the tower is not very great, so the entrainment is very low. An actual figure I cannot give you, but it is minuscule. We are not using a fluidiser.

At present we don't have fluorine recovery or rather we don't recover fluorine for commercial uses. We do scrub the gases to get out the fluorine which is in the process. The temperature of the melt is something in the region of 150°C.