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THE DEVELOPMENT OF THE HOECHST - UHDE
AMMONIUM NITRATE PHOSPHATE PROCESS.

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INTRODUCTION.

On the basis of the Odda Process (Erling B. Johnson, Odda Norway) Farbwerke Hoechst AG and the engineering company, Uhde, have developed the Hoechst-Uhde Ammonium Nitrate Phosphate Process. This development offers full scope for the production of all types of NP and NPK fertilisers and includes all processes for the conversion of byproduct calcium nitrate into calcium nitrate 15.5 % N, ammonium nitrate limestone 20.5 % N - 26 % N, ammonium nitrate 34% N, and calcium carbonate.

The development began after World War II; technical production was started in 1950. The first plant in the world for the conversion of calcium nitrate into ANL 21% was designed and built in 1955 by Uhde.

Production using the processes mentioned is of great economic importance. The use of sulphur, sulphuric acid and phosphoric acid is avoided entirely and the valuable constituents of rock phosphate, P_2O_5 and CaO, can be recovered fully in the products. The problems of gypsum waste disposal and toxic effluents, which arise in the case of phosphoric acid production from rock phosphate and sulphuric acid, do not exist.

Supplying ANL to farmers means, moreover, the complete saving of expenditure for liming soils necessary when fertilisers which do not contain calcium are used.

Difficulties from the simultaneous production and marketing of NP/NPK fertilisers plus AN/ANL fertilisers will not occur, as the amounts of N and P_2O_5 contained in these products meet the requirements of fertilisation. European agriculture uses 1.5 - 2.0 parts N per 1 part of P_2O_5 .

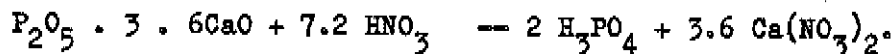
The process is most suitable as a means of overcoming the problems of NP fertiliser production arising in many parts of the world during the present, and presumably lasting, shortage of sulphur. (The demand for the nutrient sulphur, necessary for proper plant growth, could be covered by the application of gypsum, of sulphate of potash of magnesium sulphate, and is no contra-indication to the use of ammonium nitrate phosphates and AN in the fertilisation of crops).

The Hoechst-Uhde process, similarly to other developments of the Odda-Process, allows the production of NP/NPK fertilisers with up to 85% water solubility of P_2O_5 . However, a limitation to 40% - 60% water solubility of P_2O_5 is fully justified by reasons of soil chemistry of fertilisation and of technical expenditure. In Europe, water solubilities in the range 30 - 45% are accepted and the economics, both in respect of agriculture and of industrial production, provide evidence that higher figures of water solubility would not compensate very well for the higher expenditure necessary to boost the water solubility. It is the opinion of the authors of this report that a water solubility of 50% is fully sufficient for general purposes of fertilisation.

THE HOECHST UHDE PROCESS

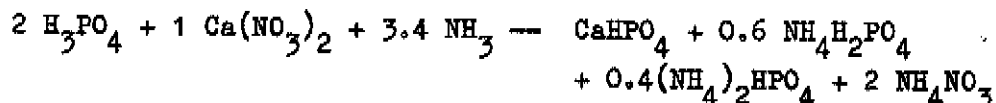
The chemistry of the process is well known and may be explained by the following abbreviated chemical equations:

Acidulation



By cooling, crystallization and separation of calcium nitrate tetrahydrate crystals, a variety of mother acids containing P_2O_5 : CaO in the molar ratio of ca. 1 : 1.3 (ca. 35% watersoluble P_2O_5 in the final NP products) up to 1 : 0.3 (85% water solubility of P_2O_5), can be produced. Taking as an example the ratio 1 : 1, the following equation shows the result after neutralization with ammonia.

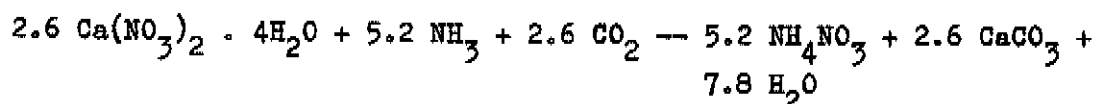
Neutralization



50% of the phosphoric acid ends in this case in the form of $CaHPO_4$ (soluble in neutral citrate solution), 50% of the phosphoric acid in the form of ammonium phosphates. The neutral NP slurry is used for the manufacture of NP/NPK products.

Calcium nitrate conversion to ANL

In the above case 2.6 moles of $Ca(NO_3)_2$ are extracted. The conversion follows the equation:



The suspension contains about 17% H_2O . After evaporation down to 3 - 8% H_2O the concentrated mixture can be granulated or prilled.

AN manufacture

The suspension of AN and CaCO_3 yields after filtration ammonium nitrate solution and calcium carbonate.

Ammonium nitrate can be used to upgrade the N content of the NP product, for manufacture of AN 34% N, or for other purposes.

Calcium carbonate

Byproduct calcium carbonate (crystal sizes from 0.02 - 0.10 mm) after drying has various applications - ANL manufacture, soil liming, artificial marble, filler for plastics, conditioner, caustic lime, neutralization. Soil liming or ANL manufacture should be given preference.

Product range and water solubility of P_2O_5

The above description of the chemistry does not explain details; however it gives evidence of the connection of calcium nitrate extraction and water solubility of P_2O_5 . Some more information can be obtained from Diagram I and from the material balance flowsheet (Flowsheet I).

Diagram I shows the composition of NP products and amounts of calcium nitrate 15.5% N and ANL 21% N in accordance with the degree of removal of "calcium oxide". Diagram I also shows the result of recycling 100% of ammonium nitrate from conversion to NP manufacture. Flowsheet I indicates the variety of products and the versatility of the production procedure for the case of 50 - 60% water solubility of P_2O_5 . The range of water solubility made possible by the process is shown in Diagram I.

The possibilities of the Hoechst Uhde process are not exhausted by the above. By introducing more nitric acid in the acidulation or to the mother acid, the recycling of ammonium nitrate from the calcium nitrate conversion to NP manufacture can be avoided. Simultaneously, a filtration can be omitted and the procedure for the direct manufacture of ANL 21% N is simplified. Also, by adding ammonium nitrate from outside the plant it is possible to upgrade the ANL to 26% N. However, these measures mean a considerable increase in the amount of N per unit of P_2O_5 produced. The amount of total N/unit P_2O_5 according to Flowsheet I is in the range of 1.7 parts by weight; this figure will climb to 2.0, even 2.4 parts N/1.0 part P_2O_5 , if surplus HNO_3 or additional NH_4NO_3 are introduced during the manufacture of NP and ANL.

The most suitable procedure can be optimised for any case. Such an optimum may involve the use of additional phosphoric acid or sulphuric acid.

From the above general information it may be seen that the Hoechst Uhde APN process gives access to a great variety of NP/NPK and AN/ANL fertilisers to cover any fertilisation programme efficiently and adequately.

THE TECHNICAL PROCEDURE

Design of plants provides conventional equipment. The plants work under remote control. Important sections of the plants - acidulation, cooling, crystallization, separation of calcium nitrate, neutralization and raw materials flow, including metering - are automated.

18 years of experience have proved the suitability of stainless steel for the acidic operations in the plant.

Acidulation

Special stirrers are used to prevent difficulties arising from foaming. Foam-breaking agents are available for cases of extraordinary froth stability.

Cooling and crystallization, separation

Agitated vessels with cooling coils. Pre-cooling with water or even with cold liquids from downstream of the plant; final cooling by brine, to be recooled by evaporation of liquid ammonia. With water solubilities up to 70% of P_2O_5 , no additional refrigeration machinery is necessary if liquid ammonia is available. Automatic centrifuges are in use for the recovery of the crystals.

Mother acid

Controlled separation of calcium nitrate; adjustment of values for P_2O_5 , CaO , HNO_3 in the mother acid. Analytical control by ion exchange and by direct titration of H_3PO_4 and HNO_3 .

Neutralization

Automated by PH control. Heat of neutralization is used for evaporation of water. PH values up to 6.3 (measured at dilutions of 1 : 50).

Pre-concentrator

NP slurries after neutralization have 8-14% water; by use of a simplified evaporator, water contents can be adjusted down to 4-5%.

Granulation

Under double shaft mixer-granulators are used for preference. One granulator can handle more than 500 mt/d of product and in some cases up to 1000 mt/d. All types of NP and NPK can be granulated, even types rich in P_2O_5 and in potash and even with sulphate of potash and additional conditioners.

The granulation equipment, including rotary dryer, sieving and mill, gives uniform granule size and works with low amounts of recycle. Density and hardness of granules are unrivalled.

The granulation equipment by reason of its great versatility is superior to prilling equipment.

In Hoechst-Uhde granulation the potash salts are reacted thoroughly with the NP slurry prior to granulation. The potash salts after granulation will not undergo any (heat evolving) disintegrating reaction. In the prilling procedure, working at a low water content of the NPK mixture, the potash salts will not undergo the necessary reactions prior to storage. Troubles during storage, in spite of the salt systems instability, have influenced the decision in favour of the Uhde mixer-granulator equipment.

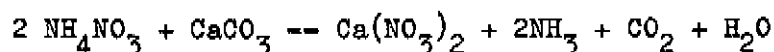
Special anti-caking agents are available with the Hoechst-Uhde process to prevent the various types of NPK and ANL from caking.

Conversion of calcium nitrate

Calcium nitrate tetrahydrate after purification is reacted with ammonia and carbon dioxide in agitated vessels or in a column. Depending on the conditions of the reaction, water content, temperature, pH values and impurities present, the two Hoechst-Uhde processes are designed to overcome all difficulties.

In the case of the recovery of ammonium nitrate by separation from calcium carbonate, the process is designed for the growth of large CaCO_3 crystals of uniform size to ensure best filtration. Both processes work at low water content.

Means are provided to evaporate water from the ANL slurry without any remarkable decomposition, according to the equation:



Granulation by pug-mills or even prilling are provided for by the developments of Hoechst and Uhde. The complete process including granulation and prilling is used in large scale technical plants to produce ANL resp. AN.

In the case of ammonium nitrate recovery as indicated in Flow-sheet I, the AN and CaCO_3 after drying and evaporation can be mixed to yield any type of ANL, etc. This, of course, is an alternative of our processes, which involves higher investment and higher consumption of energy. The versatility of this procedure opens all the possibilities of switching over to all types of NP, NPK, AN, ANL, etc., without any change of conditions in the plant.

The large scale conversion of calcium nitrate hides a lot of problems and difficulties and should not be considered as a matter of inferior importance. Experience will be required to solve the particular problems of each new project with great care. To some extent, the problems are connected with the quality of the rock phosphate used.

Final remarks and conclusions

Tables I & II and Diagram II underline the full economic importance of the Odda process and its technical development. Including the necessary nitric acid plants, the whole Hoechst-Uhde APN plant, including AN/ANL manufacture represents a cheap investment. The savings in sulphur at present quotations are high enough to pay for the investment within 3 years ! The investment itself is not higher than that for plants using sulphuric acid and phosphoric acid in the production of ammonium nitrate/phosphates.

The nitric acid route of NP manufacture is very suitable for meeting the fertiliser demands, equally for phosphatic and nitrogenous fertiliser, in any part of the world where ammonia and carbon dioxide are available. Although the concentrations of fertilisers produced by other processes using urea and DAP are higher, the products delivered from Odda plants are concentrated enough for transport over great distances.

Further developments are presently under way. It may be predicted, that these developments will not result in lower cost of investment and production, but will render APN manufacture independent of carbon dioxide and may result in higher product concentrations. The target is still to save sulphur and to produce efficient phosphatic fertilisers at the lowest cost.

TABLE I

The following figures show:-

- (a) consumption of sulphur,
- (b) waste products,
- (c) credit for CaCO_3 used for ANL manufacture,
- (d) expenditures for liming of soils, in a comparison of the following processes:
- (x) NP products compounded of $(\text{NH}_4)_2\text{SO}_4$ and DAP 18:46:0
basis: sulphuric acid - phosphoric acid
- (y) NP products compounded of NH_4NO_3 , CaHPO_4 , DAP
basis: sulphuric acid, phosphoric acid, nitric acid
rock phosphate
- (z) NP products equal to y) manufactured however by the
Hoechst Uhde process on the basis of : nitric acid,
rock phosphate, carbon dioxide.

figures per 100 mt P_2O_5 + 100 mt N

NP processes	(x)	(y)	(z)
a) sulphur consumption	185 mt	60 mt	0
b) gypsum waste	450 mt	260 mt	0
c) amount of CaCO_3 credited in case of use for ANL manufacture	0 mt	0 mt	160
d) amounts of CaCO_3 necessary for liming of soils	ca.150	ca.40	ca.40

Hoechst-Uhde Odda-Process (z) provides the most attractive figures.
Cautiously estimated, DM 14.000/100 mt P_2O_5 can be credited in favour
of the Hoechst Uhde process !

TABLE IIData for economic evaluation of the Hoechst - Uhde processRaw materials/100 mt P_2O_5 + 170 mt N in the products

Rock phosphate 77/76 BPL	ca. 280 mt
Nitric acid 60%	635 mt
Ammonia neutralization + conversion	110
Carbon dioxide	80 mt
(total ammonia)	213 mt

Utilities and labour/100 mt P_2O_5 + 170 mt N in the products

Steam l.p.	420 mt
Steam h.p.	67 mt
Fuel gas	50×10^6 kcal
Fuel oil	130×10^6 kcal
Cooling water 20°C	$14,000 \text{ m}^3$
Electric power	max. 65,000 kWh
Cooling brine	30×10^6 kcal
(recooling of brine by evaporation of liquid ammonia)	
Compressed air	$20,000 \text{ m}^3$
Labour	480 hours

Investment cost including erection and buildings:

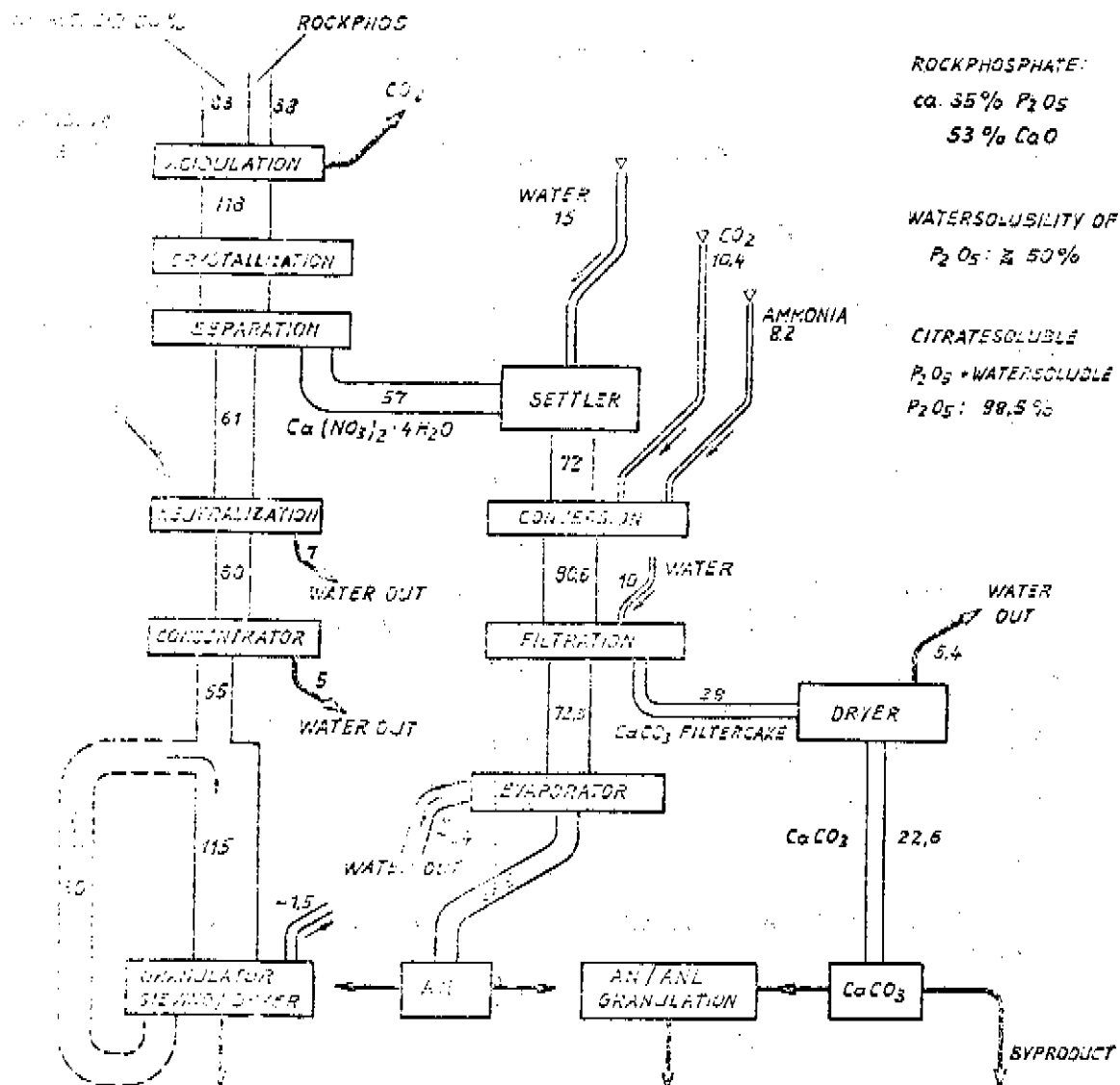
Nitric acid plant)	
NP/NPK plant)	
Conversion plant)	ca. DM 28 millions
AN evaporators)	- battery limits -
$CaCO_3$ dryer)	

Investment for a 200 mt P_2O_5 /d plant will be approximately DM 53 millions.

FLWSHEET I

HOECHST-UHDE AMMONIATE PHOSPHATE PROCESS

Materials flow According to manufacture of NP 16/25/0 and alternatives possible by use of AN for N-upgrading of NP-products



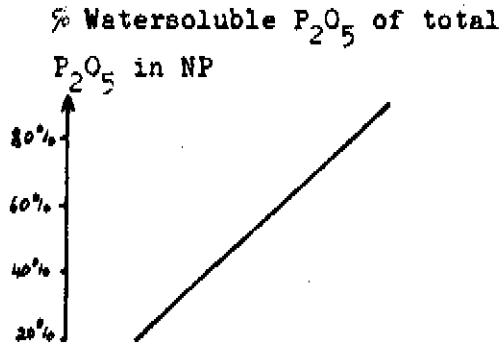
a) NP 16/25/0
400 000 mt/y
b) NP 23/20/0
200 000 mt/y
c) NP 24/15/0
877 000 mt/y

b) and c) are
EXAMPLES
for use of
AN

a) ANL 25% N
375 000 mt/y
b) ANL 26% N
240 000 mt/y
c) nil

a) CaCO₃
66 000 mt/y
b) CaCO₃
101 000 mt/y
c) CaCO₃
164 000 mt/y

DIAGRAM I - HOECHST UHDE APN PROCESS



Attention : all figures are roughly calculated and may change dependent on types of rockphosphate, on amount of HNO_3 used etc.

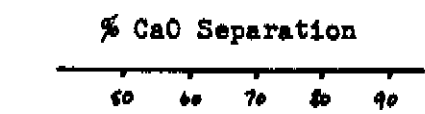
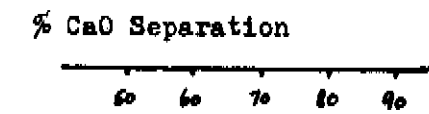
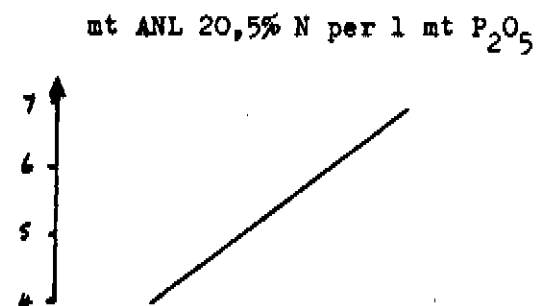
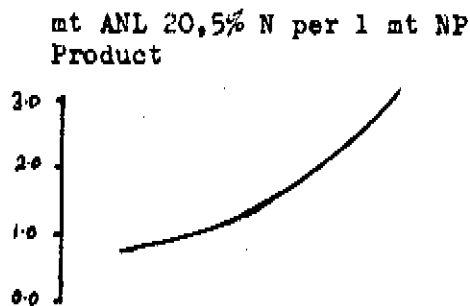
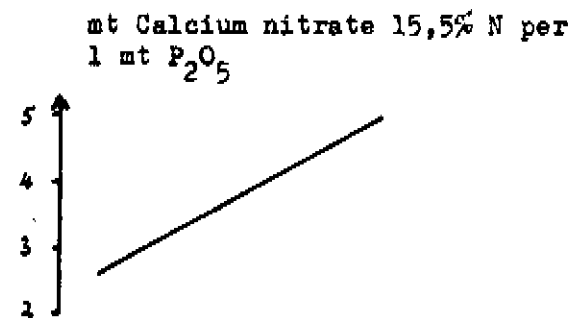
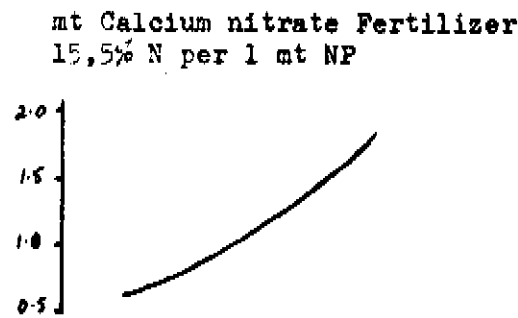
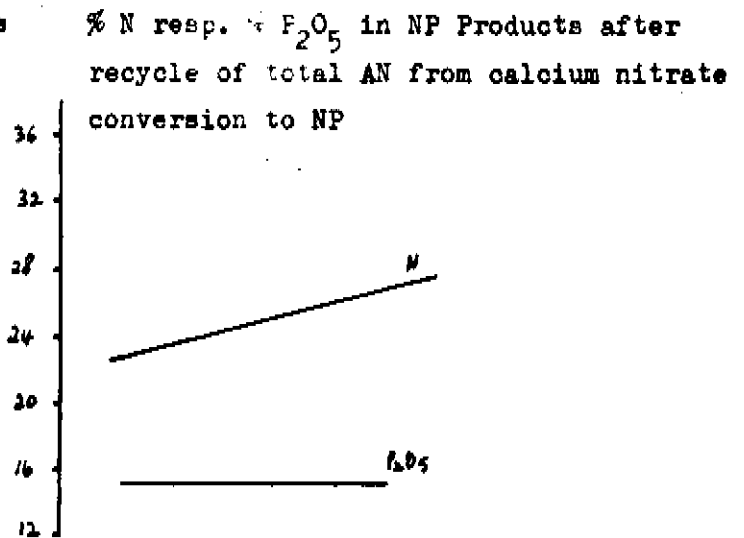
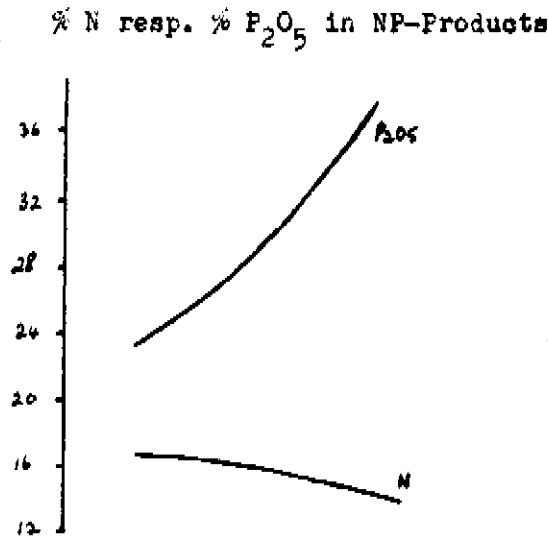
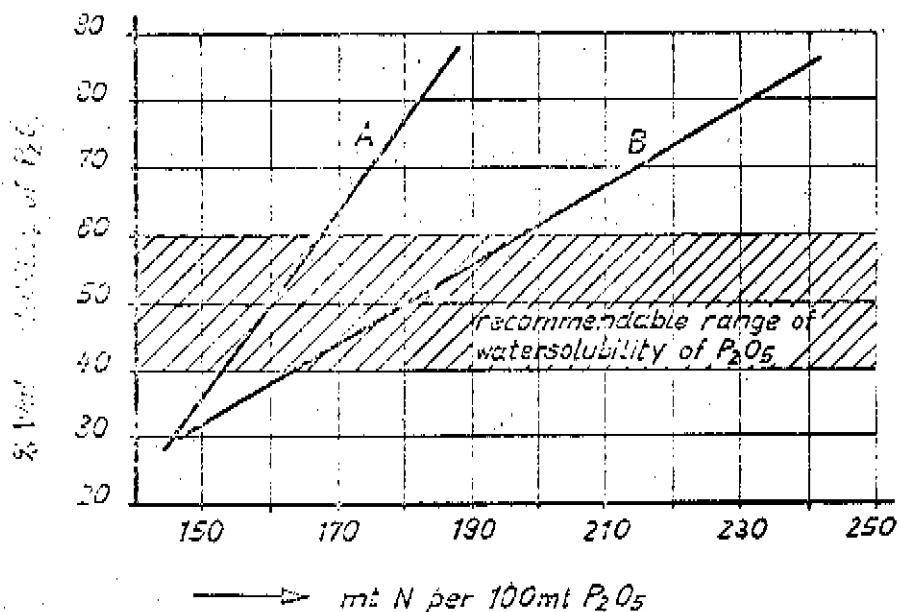


DIAGRAM II
APPROXIMATE AMOUNTS IN mt N CONTAINED
IN THE NP + ANL PRODUCTS



- A) No additional use of HNO_3 ; AN from calcium nitrate conversion can be recycled to upgrade N content of NP-products. All types of NP-products can be produced
- B) Additional use of HNO_3 to produce NP fertilizers of the 1:1 type and use of total AN from conversion of calcium nitrate for manufacture of ANL 20.5%N. CaCO_3 -byproduct can be avoided

DISCUSSION

DR. H. BANTHIEN (Hoechst-Uhde, Germany): The Odda process is well known to all of you. To avoid being immodest about what I am now presenting to you, I should mention that apart from Norsk Hydro, Badische Anilin was also very early in the development of this process and achieved excellent results. Somewhat later in the chronological sequence came Farbwerke Hoechst, again with a somewhat modified development which for a number of years proved rather difficult in its technical operation but which today has solved all its teething troubles. In addition, I should mention Chemische Fabrik Kalk as the second Germany company to devote considerable effort to this process and as one of the first companies to operate the conversion of calcium nitrate to ammonium nitrate and calcium carbonate. Also, I saw myself at a very early date the remarkable plants of the Dutch State Mines, and you all know that basic questions relating to the calcium nitrate separation and the complicated phase diagram were worked out and demonstrated there.

The Odda process has great advantages, particularly with regard to the low P_2O_5 costs of production. The complete avoidance of sulphur is, in my view, still one of the important factors in the achievement of low costs. The papers which have been presented to this conference have somewhat neglected to bring out the importance of the simplest form of the Odda process, i.e. to manufacture calcium nitrate fertiliser from the by-product calcium nitrate.

If one considers the figures in the latest estimates of world fertiliser consumption of the TVA and if one assumes that only half the quantity of P_2O_5 stated for 1970 will be used and that this P_2O_5 will be manufactured using sulphur to make phosphoric acid, ammonium phosphate, etc., then this would require an expenditure of the order of \$1,000 million per year at current sulphur prices.

I was conscious that it would be difficult for me to bring something new to this discussion. In my paper, I have therefore presented a series of diagrams from which the interested reader can determine what quantities of calcium nitrate arise for a given water solubility and also what quantities of calcium ammonium nitrate are available after conversion. You will see from these diagrams that the Odda process is really very flexible and requires no special technical efforts if production is restricted to medium water solubilities. But you also see from these figures which are in direct weight relationship with the P_2O_5 , that such a process can only be used to advantage when an actual market exists for these fertilisers. If one limits oneself exclusively to calcium nitrate, the by-product calcium nitrate occurs to give an N : P_2O_5 weight ratio of 1.3. In the most favourable case, this ratio rises to 1.6-1.7 with the conversion of calcium nitrate to calcium ammonium nitrate. This does not mean to say that substantially higher quantities of nitrogen cannot be obtained if things are somewhat simplified and if, for example, one does without the separation of the ammonium nitrate and calcium carbonate.

Technically, the Odda process and those who practise it are somewhat enveloped in secrets. This is understandable because the companies using this process derive a genuine profit from these matters. In relation to the P_2O_5 cost of production, the advantage compared with other processes is quite considerable. But I say here and now that any young technician or chemist who knows how to handle ammonium nitrate and such things should not

be afraid to take and examine such a process himself. At any rate, when I began with the development of this process at the end of the second world war, I had no great apprehension about doing it and I did not find the difficulties particularly great. I can also tell you that when the first conversion process for the manufacture of calcium ammonium nitrate from calcium nitrate was developed and constructed at Scholven-Chemie in Germany by Uhde for the first time in the world, I had only four months to develop this process with two other chemists of Farbwerke Hoechst.

I do not wish to imply that experience is easily attained, but I will say that it would be fine if today our young chemists and engineers were able to bring out something new in the field of P_2O_5 fertiliser production costs. It should interest you to know that in the process described in my paper there is no difficulty in achieving a P_2O_5 yield of roughly the theoretical maximum of 100%. Losses occur only from leakages from some part of the plant. Naturally, this 100% yield, or 100% conversion to phosphoric acid, requires extraction of the P_2O_5 from the calcium nitrate. I would say that with the remarkable crystallisation processes which are operated today, P_2O_5 losses are now very slight and certainly do not affect the economics of the process. It remains true that the Odda process and all who have contributed to it have achieved a very worthy result. I also think that this process will account for an increasing volume of phosphate fertiliser production.

MR. A.H. MØLLER (A/S Dansk Svovlsyre - og Superphosphat Fabrik, Denmark): Many processes have been developed originating from the thoughts and work of Erling B. Johnson, Norway, and a look at the list of papers given at the technical conferences of ISMA will underline that these processes have had the full attention of the members.

Today we have in front of us Dr. Banthien's paper: "The development of the Hoechst-Uhde Ammonium Nitrate Phosphate process", which has been a very interesting paper to read.

There are, however, some points, which I should like to have clarified, and I have some questions for Dr. Banthien.

You write on page 2 that with the Hoechst-Uhde process you are able to produce NP/NPK fertilisers with up to 85% water-solubility of the P_2O_5 -content. I should like to know whether that figure is considered maximum and why?

On the same page you say that you cool, crystallise and separate the reaction mixture. Do you filter the reaction mixture before cooling?

It would also be interesting to know how big are the P_2O_5 -losses in the calcium nitrate.

On page 4 you mention defoamers. Which agent do you normally use when working on a Morocco 75/77-basis?

Later, on the same page you speak about the granulation and the admixture of additional conditioners. What do you understand by the expression conditioners? And what is your experience regarding the addition of micro-nutrients, for example blue vitriol or copper? The granules are said to be uniform in size and unrivalled in density and hardness. But then how are the spreading properties in a spinning disc distributor in the fields, compared with for example prilled or spherodized NPK?

On page 5 anti-caking agents are mentioned. Which anti-caking agents do you use, and is it different agents for the different NPK-formulations?

If we take a look at the economic evaluation of the Hoechst-Uhde process in table II, where Dr. Bantien calculates the raw materials consumption per 100 t of P_2O_5 and 170 t of nitrogen in the products you will find that the efficiency regarding P_2O_5 has been between 101,2 and 102,5 per cent and the overall losses in the nitric acid-plant and NPK-plant have been as low as 3.4%. How do you come to these figures?

DR. H. BANTHIEN: In the experiments which we conducted between 1950 and 1955, we made particular efforts to achieve high water solubility. We established then that it is difficult to exceed 85%. Experimental products of a composition of roughly 15-30-0 were produced with a water solubility of about 90%. Later, there proved to be no need for this high water solubility, particularly in German agriculture. Moreover, the economics were not very interesting. This has all come under discussion after our unfortunate experience of one or two unpleasant cases of self-sustaining decomposition of the fertiliser. In my view, agriculturally speaking - and I am no agronomist - the high water solubility is not justified. I think it is difficult to go above 85% water solubility.

With regard to the question as to whether we should filter before cooling, or whether we do filter before cooling, we do not filter, but precautions are taken with silica-bearing phosphates which enable a large part of the silica to be separated off.

The P_2O_5 content in the calcium nitrate tetrahydrate after separation of the mother liquor depends on whether scrubbing is done or not. If it is washed, the P_2O_5 content in the calcium nitrate tetrahydrate is about 0.5% in terms of salt. In any case, one can reduce and extract the phosphate in further processing and thus avoid losses. During the reaction, in the case of Morocco 75-77% BPL phosphate, defoamers are not necessary. With the use of agitators which break up the foam, difficulties are not encountered with these phosphates. There are various defoamers, and I cannot say which we use, but they are very simple substances.

Farbwerke Hoechst have produced, and still do produce complete fertilisers containing trace elements. We have not introduced any particular discussion of the experiments which have been made so far as to whether individual trace elements should be added in specially high quantities, but there are no serious objections to this.

The granule size distribution of the products from our plants corresponds roughly to what one can expect statistically from a double wave granulator, and I think that the distribution on the field, using spinning disc applicators, is roughly the same as with a prilled product.

There are various anti-caking agents which prevent the compaction of the fertilisers. There is much talk of amines, and Kieselgur is used, and also oiled ground limestone. This depends often on local conditions. As far as the various NPK forms are concerned, I am rather inclined to think that formulations rich in ammonium nitrate require somewhat greater protection.

MR. A.H. MØLLER: What is the explanation of the 102% yield?

DR. H. BANTHIEN: That must be an inaccuracy in the revision of these figures. I believe the table shows 280 metric tonnes of phosphate 76/77 BPL. If you substitute 285-287, then I think these figures are alright. With regard to the nitrogen, I must say that if one takes account of both the ammonia and the nitric acid, my figures seem to be about right, for according to my calculation we get a total yield of 92%. Only the figure of 3.4% seems to me too small. This 92% includes the losses in the nitric acid production, assuming, of course, a good modern plant.

MR. A.H. MØLLER: I have calculated that 635 t of nitric acid at 60% should be about 85 t of N, and then you have ammonia neutralisation and conversion of 110 t and this is equal to 91 t of N. That gives a total of 176 t, equal to 213 t NH₃ and then you have a loss of 6 t of N on 176, that is 3,4%.

DR. H. BANTHIEN: I must again apologise for such bad figures. However, they suffice for an approximate economic calculation, and the cautious chemist or engineer will generally add something into such figures, in any case.

MR. J. FRÖCHEN (Pierrefitte, France): I should like to put four questions to the author:-

- 1) On page 5, he describes a pre-concentrator consisting of a simplified evaporator. What does he mean by a simplified evaporator?
- 2) On page 6, he mentions a low rate of re-cycle. What does "low" signify?
- 3) On page 7, he mentions sulphur economies corresponding to a three year amortisation of investment. What does he mean by amortisation in three years? Is it the total depreciation or the depreciation of the excess equipment necessary in order not to use sulphur?
- 4) On page 7, he mentions the manufacture of APN independently of carbonic anhydride. Can he give us some details in this regard?

DR. H. BANTHIEN: One can use normal evaporators for pre-concentration, and I think that Mr. Lie's remarks during the discussion of the previous paper revealed that such evaporators are in use. By a very simple evaporator, we mean a disc apparatus which is operated directly by hot gases. Such units are, for example, in use at Scholven-Chemie and also in other companies.

With regard to the second question, our plants use screw granulators. It has been demonstrated that high concentration and high temperatures during the granulation process are very advantageous for the usual NPK fertilisers containing ammonium nitrate. There is an old I.C.I. process concerning the separation of the oversize before the dryer. If one uses something of this sort with NPK fertilisers and makes a corresponding simple adjustment, one arrives at very low re-cycle ratios of roughly one part re-cycle to one part product. At the same time, this step, together with pre-concentration to a very low water content, means a very high throughput per unit of granulation plant.

With regard to the third question concerning my remark that "the savings in sulphur are high enough to pay for the investment within three years", I mean that with a fertiliser produced from ammonium sulphate and ammonium phosphate a considerable amount of sulphur must be used. If, in contrast, no sulphur whatsoever is used in the Odda process, then one can pay for the investment for three years running out of the savings which occur through not buying any sulphur. I would only add that if I did not have to add phosphoric acid to produce a product of similar water solubility to that in the Odda process, the period would not be 3 years but 6 or 7.

The development of new processes which do without carbonic acid and yet have as similarly favourable a result as the Odda process is unfortunately not yet completed.

MR. S. STRELZOFF (Chemical Construction Co., U.S.A.): I read in this paper that Hoechst claims to be one of the first companies in the world to convert calcium nitrate to ammonium nitrate. In fact, we did it 33 years ago here near Liege.

I should like to put a question: at what temperature do you cool to obtain the crystallisation of the calcium nitrate? What is the distribution of the fluorine from the phosphate, as between atmospheric effluent and what remains in the product?

DR. H. BANTHIEN: The question of temperature and cooling is important. To achieve 60% water solubility, it is sufficient to have temperatures which may still be above 0°C. In fact, I believe a temperature of 5°C is quite sufficient to give this water solubility.

Secondly, with regard to the fluorine, depending on the temperature of the reaction, we get a small quantity of fluorine. For example with a reaction temperature of 50°, we get rid of only 5% of total fluorine, but with a temperature of 70°, as is practised in several plants, I estimate that 25 to 30% of the fluorine is eliminated. All the remaining fluorine remains in the solution and comes finally into the NP or NPK product in the form of calcium fluoride and similar fluorine compounds.