

ISMA* Technical Conference

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

DISCUSSIONS

1st Working Session: Physical properties of fertilisers in relation to granulation, distribution and transport.

TA/76/6 Granulation as an equilibrium process by J.H. van der LEEK, UKF, Netherlands (Rapporteur J.D. CRERAR, Fisons Ltd, UK)
Presented by Mr. C. HOEK (UKF, Netherlands)

Q - Mr. I.K. WATSON (UKF, UK)

A - Mr. HOEK explained that the sieve analysis of a granulate is determined by the standard method. Any lumps or agglomerates that can be broken by just finger pressure will break, thus avoiding errors caused by slight caking of the granulates being taken as strongly agglomerated large granules.

Q - Mr. S.B. PARIKH (GSFC, India) asked about the formation of lumps when moisture content is excessive in the production of DAP.

A - Mr. HOEK pointed out that the paper referred to the ammoniator-granulator rather than the blunger experienced by Mr. Parikh. However a similar problem was known to him, and could be avoided in two ways:-

a- increase the recycle to decrease V/G.

b- reduce the moisture content of the feed. For DAP this can be achieved by running the pre-neutraliser at a $\text{NH}_3:\text{P}_2\text{O}_5$ mole-ratio of 1.4 which corresponds with the highest solubility of the ammonium phosphate slurry.

Q - Mr. O.H. LIE (Norsk Hydro, Norway)

A - Mr. HOEK explained the plant control scheme. UKF had automated the traditional sieve analysis test method, and it operated 6 to 8 times per hour. A print out of the results was used for plant control by the operators. For high granulation efficiency processes there was a benefit in speeding-up the result of the sieve analysis. UKF was developing an optical system to measure sieve analysis.

Q - Mr. R. MONALDI (Montedison, Italy) mentioned that Montedison had increased production rate by 30% by using surfactants.

A - Mr. HOEK, UKF had tested surfactants and the results were such that the technique had not been commercialised.

Q - Mr. T. MCCARTHY (NET, Ireland)

A - Mr. HOEK did not have a special technique, but calculated it from the granulation conditions, e.g. temperatures, H_2O content, and a knowledge of the phase diagrams.

Q - Mr. K.D. SHAH (ICI, UK) asked whether UKF had experienced the process of granulation continuing in the front-end of the drier.

- A - Mr. HOEK agreed that, with a short retention time in the granulator and/or unreactive constituents, equilibrium is not reached in the granulator. Under those conditions granulation in the drier may occur. Also fine material may agglomerate in the drier.

TA/76/7 Quantitative X-ray analysis of crystalline components in fertilisers by C.G. VONK, DSM, Netherlands (Rapporteur J.D. CRERAR, Fisons Lt, UK)

Q - Mr. P. MORAILLON (Gesa, France)

- A - Mr. VONK agreed that neither pure NH_4NO_3 nor KNO_3 were found in nitrate fertilizer, only a solid solution of the two salts. Mr VONK said that the double salts $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ did exist but could not be isolated in a sufficient degree of purity to be included in Table 1.

In reply to a further question by Mr. MORAILLON, Mr. VONK felt that break-down of granules could be due to substitution of K by NH_4 . However in the samples examined this break-down was confined to roughening of the surfaces and some bridge formation which was probably responsible for caking.

Q - Dr. P.F. KAVANAGH (NET, Ireland)

- A - Mr. VONK gave details of the critical method of sample preparation. The sample was ground in a mortar under an inert liquid (usually CCl_4) to a particle size of less than 10 micron; the mortar was placed in a glovebox which was flushed with dry nitrogen in order to prevent water uptake. Next the sample was transported to the diffractometer in a closed box. The sample chamber in the diffractometer was constantly flushed with dry helium (helium is here preferred to nitrogen because of the lower scattering). As a result the sample was not allowed to come into contact with water vapour at any time after it has been taken from the container in which it had been transported.

The reliability of this procedure had been tested by applying it to a mixture of KCl and NH_4NO_3 , which was very sensitive to water vapour. If prepared without any precautions it had been found to have reacted completely to give KNO_3III , KNO_3II , $\text{NH}_4\text{NO}_3\text{III}$ and NH_4Cl .

Leaving out the CCl_4 during the grinding had led to a low degree of conversion into these compounds, whereas on application of all precautions no reaction had been observed at all.

Q - Mr. O.H. LIE referred to the fact that there was a family of crystal faces that would give the same NPK ratio and asked about the accuracy of Table 4 (a) and (b).

- A - Mr. VONK replied that the number of combinations of the components having a certain N, P and K content was restricted by the requirement that these elements have to be incorporated into the compounds that had been observed.

In fact, only those combinations could be thought to occur which can be obtained by all (hypothetical) reactions leading to a redistribution of the observed components, without material transport either to or from the sample. (One might think of these as the solid state reactions that can proceed within the sample). Each of these combinations corresponded with a certain combination of deviations of the component concentrations from the true values. The deviations in the X-ray values could however be considered to be distributed completely at random; therefore the chance that these deviations corresponded with one of the combinations leading to the same N, P and K contents was extremely small.

The comparison of the N, P and K concentrations was very useful, as these figures usually are available with great accuracy.

Q - Mr. B. RAISTRICK (Cremer & Warner, UK) commented that the X-ray method was most useful when the chemical method was impossible. He also asked what experience DSM had of small crystallites being too small to diffract.

A - Mr. VONK replied that DSM had experienced small crystals giving a variation in the intensity ratios of different lines, but complete absence of a line was not expected.

TA/76/8 Hygroscopicity of fertiliser materials by P. HEGNER and L. JAGER, Research Institute of Inorganic Chemistry, Czechoslovakia (Rapporteur J.D. CRERAR, Fisons Ltd, UK)

Q - Mr. P. MORAILLON (Gesa, France)

A - Mr. HEGNER discussed the method of measurement of relative humidity by the lithium chloride element. The method had been published and known for about 4 years. The sample of fertilizer was submerged in a cell with the lithium chloride element in a thermostatic bath. Results were taken repeatedly to ensure the correct temperature had been achieved.

Q - Mr. O.H. LIE (Norsk Hydro, Norway) pointed out that the interesting range of moisture content for commercial fertilizers was 0.3 to 2.0%. He asked about the kinetics of water absorption in that range.

A - Mr. HEGNER replied that in connection with assessing the effectiveness of coating materials his Institute had commenced an investigation into the thermodynamics of moisture uptake.

Q - Mr. I. WATSON (UKF, UK) asked if Mr. HEGNER was extending his studies to the diffusion process occurring in a drier.

A - Mr. HEGNER felt that drying rate was determined by parameters connected with the air, especially velocity, and the ratio of solid: gas in the drier. This was a subject he would like to study further before making detailed comments.

TA/76/9 Product quality requirements in bulk shipment of fertilisers by O. KJOEHL, Norsk Hydro, Norway (Rapporteur Mr. O.H. LIE, Norsk Hydro, Norway)

Q - Mr. I.K. WATSON (UKF, UK)

1. Are all the NPK formulations in Table 4.1. based on ammonium nitrate?
2. The conclusion of Table 5.2.1 is that a parting agent plus a surfactant should be used to get good anticaking results. However, Fig. 6.1.1 indicates a possibility for high a dust forming effect for this combination. Which do you consider the more important criterion: caking or dust; and what is your solution to these apparently conflicting objectives?

A - Mr. O. KJOEHL

1. Yes
2. We regard caking as more important than dust. However, the dust problem can in many cases be solved by using dust suppressants.

Q - Mr. K.D. SHAH (ICI, UK) and Mr. P. MORAILLON (Gésa, France)

Is it possible for the author to elaborate more on the subject of the nature and use of surfactants and dust suppressants mentioned in the paper?

A - I regret to say, but we consider this proprietary knowledge.

Q - Mr. P.L. BALDWIN (Cremer & Warner, UK)

You mentioned the effectiveness of amorphous silica as a parting agent. What is your source of such material on a commercial scale?

A - The amorphous silica I refer to in the paper is a by-product from the steel industry.

Q - Mr. K.D. SHAH

1. The dust level figures given in Table 5.1.1 appear to be high. Was oil or any similar "adhesive" used on the granules in the test?
2. Referring to section 5.3 on the caking of newly produced NPK, how important do you regard the initial caking during the first 3 to 4 weeks and the subsequent reduced tendency to caking of the material rendered free-flowing in terms of the shipping operations? Is it your standard practice to store NPK fertilizers for 3 to 4 weeks before shipping?

A - 1. No oil or other dust suppressants was used on the granules. The figures in Table 5.1.1 therefore express the ability of the different parting agents to adhere to the fertilizer particles.

2. Our experience is that the tendency to caking is highest during the first 1 to 2 weeks after production. The main reasons for this are postreactions in the granules and - because the newly produced

NPK usually is warmer than the surroundings- that water vapor diffusion from the core to the surface of the pile takes place. After about 2 weeks storage these reactions have stopped, and with NPK we have in the last years experienced no caking problems in the holds of the ship.

Q - Mr. D.J. HUIJGEN (UKF, Netherlands)

Your paper shows that dust formation is greatest when you are using both parting agent and surfactant. Is this true for all types of surfactants?

A - We have tested fatty amines and some alkyl sulfonates and have found that at least all these increase dust formation.

Q - Mr. C. GOLOMB (Omnia Fertilizers, South Africa)

Could the author give more information on the sieve analysis of the various anti-caking agents?

A - Our experience is that the particle size of the parting agent should be less than 10 micron. The anti-caking effect and the ability to adhere to the fertilizer particles usually increase with decreasing particle size of the parting agent.

Q - Mr. G. LANGHANS (Hoechst, Germany)

You have determined that in NP fertilizers the particle strength is not changed by a water uptake of 1%. You state that this effect is caused by the lack of water penetration into the interior of the particles. I think another interpretation is also possible: in NP fertilizers made by the Odda-process, the water insoluble components have a large surface. BET-measurements show a value of about 50 m²/g. At first water penetrating the particle is adsorbed on these surfaces. By further increase in the water uptake, ammonium nitrate will eventually go into solution with a resulting loss of particle strength.

I would thus consider the water insoluble components of the fertilizer as a "drying agent". During drying of the fertilizer these components will lose water and become activated.

A - We have found that NP fertilizers with high contents of NH₄NO₃ have low porosity and that the main portion of the water pick-up condenses on the surface of the particles. Here the moisture dissolves NH₄NO₃, which results in wet particles with poor flow properties. The particle strength, however, is not much affected.

Q - Mr. D. CRERAR

From your slides it appears that the bulk vessels employed are of an exceptionally high standard. Can you indicate the rate of rejection of ships due to low standard?

A - When selecting vessels for bulk shipment we cooperate closely with our Shipping Department. We always look for high standards vessels. At the negotiation step, I would say that 10 to 15% are rejected due to low standard.

Q - Dr. W. BOOS (Gewerkschaft Victor, Germany)

1. The results in your paper refer to prilled products. Have you made similar studies with granulated products?
2. Is there a change in the water content during prilling?

A - 1. With regard to caking and water content, we have found no difference between prilled and granulated products. Our requirement is that the water content should be between 0.4 and 0.6% in NPK's high in nitrogen. For NP's and NPK's low in nitrogen we allow up to 0.7% H₂O.

2. Normally there is no change in water content during prilling operation.

At the end of the discussion the following statement was made by Mr. Van Heyfte of CNA, Netherlands.

"CNA has completely solved the caking problems of urea and CAN. We obtain free-flowing products for at least 6 months in piles of 5000 tons, absolutely free of dust and ammonium odour. The products are exported in bulk to all parts of the world".

TA/76/10 Improvement of physical properties of fertilisers with special reference to bulk distribution and pallet handling by J.W. BAYNHAM and A.M. McLEOD, Scottish Agricultural Industries, UK (Rapporteur O.H. LIE, Norsk Hydro, Norway)

Q - Mr. I.K. WATSON (UKF, UK)

1. Have you used intermediate bulk containers for AN-based compounds at all and, if so, has it been successful?
2. Many companies have given up the use of shrink wrapping due to present high costs of plastics. Have you considered alternatives to shrink-wrap (e.g. bonding, loose returnable covers), and how do you justify its cost?

A - Mr. J.W. BAYNHAM

1. Yes, but to a limited extent. We are in a process of continuing development of this phase.
2. The cost of shrink wrapping has to be compared with the alternative methods for protective storage, either by the producer, the supplier or the customer. We have considered alternatives. At the present time, however, shrink wrapping presents the most economic way of storage for all concerned. In our experience returnable covers are not returned.

Q - Mr. C. KELETI (UNIDO, Austria)

1. Portable fertilizer bulk containers (2 ton) as shown in Fig. 1 if accepted by the farmers could result in "on farm storage", reducing capital investment tied up in storage buildings by the producers. Please comment.

2. Are the portable containers weatherproof, and reusable if carefully handled?

A - Mr. J.W. BAYNHAM

1. This is what happens in practice. The supplier finds himself involved in capital investment required by portable storage on the farm. This is not attractive to the producer/supplier.
2. The portable containers have to be weatherproof and the required construction is such that they are reusable.

Q - Mr. P. ROLFSEN (Norsk Hydro, Norway)

How does the economy of bulk container distribution compare with all bulk handling, and how many times is such a container used in one season?

A - Mr. J.W. BAYNHAM

The answer is not a direct one but the result inevitably is dictated by what the customer wants and is willing to pay for. In our case he is willing to pay a premium, or additional cost, to obtain the palletized unit load. With its introduction bulk demands have reduced dramatically.

Q - Mr. A. KABIL (Donau Chemie, Austria)

What is the average storage time of the products prior to use?

A - Mr. A.M. McLEOD

The storage time of the products is dictated by two factors:

- a) The market structure and the pricing policy.
- b) The production capacity relative to the market requirement.

In our case in the UK the conditions are such that, recognizing that averages can be misleading, our average storage time must be between 6 and 9 months.

At this point Mr. W.H. COATES (Albright & Wilson, UK) invited the audience to express their views on the average storage time of fertilizers in other countries. No one seemed inclined to answer and the chairman of the session, Mr. D.J. HUIJGEN (UKF, Netherlands) directed the question to Mr. M. WILLEMS of UKF who answered:

Mean storage time of fertilizers on the European continent depends on whether it is used in the domestic market or exported. Speaking for my company, UKF-Netherlands, I may say that a typical domestic product like 14-14-14 has an average storage time of about 6 months, whereas the average storage time of products that show significant export figures is in the order of 3 months.

Q - Mr. K.C. KNUDSEN (Superfos, Denmark)

You state on page 174 that introduction of Stakpak resulted in bulk delivery being very much reduced. Is that due to convenience for the

farmer or due to lower costs? In other words: How do the total costs of Stakpak delivery compare to total costs of bulk delivery in Scotland?

A - Mr. A.M. McLEOD

Again the answer must be what the customer wishes and is willing to pay for. With the introduction of Stakpak our sales of bulk material have dropped dramatically, and the customer pays the premium cost for the Stakpak.

Q - Mr. J. DONEGAN (Goulding, Ireland)

1. What is the breakage rate of the plastic bags between packing line and the customer?
2. How significant is the cost of the pallet in the overall packaging cost?
3. How do you handle the repair of the pallets?

A - Mr. J.W. BAYNHAM

1. At the packaging unit the breakage is 0.3% while the overall breakage from the point of packing to customer is about 1.5%.
2. As we charge our customers for the pallets on which we deliver shrink wrapped unit loads and credit him on its return in good condition, the cost of the pallet system is limited to the cost of repair and recovery.
3. We inspect and repair pallets as they are returned to our packing unit. Occasionally, pallets which should have been repaired slip through the system and are used when they should not have been, as, I am sure, happens with many other companies.

Q - Mr. O. JENSEN (Superfos, Denmark)

How much of the products do you have to take back because of caking problems?

A - Mr. J.W. BAYNHAM

In our paper we discuss the necessity of having a high quality, free flowing product. Yes, we have had some caking problems. We are sure that there is no one here to-day who has not had this experience. In our case the problem is a very minor one, otherwise the system would be unacceptable.

Q - Mr. T.C. LOEWY (Fertilizers & Chemicals, Israel)

Is there any opposition to the use of plastic bags because of problems caused by slippery bags?

A - Mr. J.W. BAYNHAM

We do experience some problems with bag slip with polythene bags. In these cases we use hot melt adhesive to overcome the problem. We believe this really is a problem to be studied by the plastic film manufacturers since it is concerned with the coefficient of friction, especially with printed film.

2nd Working Session: Phosphate rock and phosphoric acid

TA/76/16 : Utilisation of difficult phosphate ores by T.P. HIGNETT,
E.C. DOLL, O.W. LIVINGSTON & B. RAISTRICK, IFDC, USA
(Rapporteur W.E. DUMOIS, ERT, Spain)

Q - Mr. S. ORMBERG (Norsk Hydro, Norway)

What is the relative cost of Ferralium as compared with 316 or 317 stainless steel and high nickel alloys such as UB6 and HV9?

A - 1. Ferralium alloy

Castings: 5.5. to 6.5 U.S. dollars per kilogram.

Plate: 4 to 5 U.S. dollars per kilogram, depending on thickness.

2. 316-type stainless steel: about 20 percent lower.

3. UB6 and similar high nickel alloys: 15 to 30 percent higher.

Q - Mr. W.E. DUMOIS

If you let the iron and aluminium from the phosphate ore end up in the fertilizer as phosphates, do you have any experience with regard to the agronomic effects of such compounds?

A - TVA has made extensive agronomic tests of fertilizer produced from Florida leached zone ore in which about half of the P_2O_5 is present as aluminium phosphate (1). The remainder of the P_2O_5 was present as ammonium phosphate and dicalcium phosphate. Products containing 20 to 30 percent of the P_2O_5 in a water-soluble form were about equal in effectiveness to triple superphosphate both in initial and residual response (3 crops). Products containing only 4 percent of the P_2O_5 in a water soluble form were initially less effective, but the residual effectiveness for the second and third crop was equal to triple superphosphate.

Huffman (2) reported that water-soluble fertilizers (superphosphate) rapidly formed insoluble iron and aluminium phosphates in acid soils, sometimes complex compounds. The agronomic value of these compounds varied with their crystallinity, composition, and the type of soil on which they were tested. Crystalline iron phosphate (strengite) and crystalline aluminium phosphate (variscite) were nearly worthless on acid soil, but nearly equal to monocalcium phosphate on calcareous soils. Amorphous iron and aluminium phosphates were 60 to 70 percent effective as monocalcium phosphate on acid soil and more effective than monocalcium phosphate on calcareous soil.

Q - Mr. M. BONGARD (Windmill Holland, Netherlands)

You talk about using Hi - Fe/al ore in your paper. Please could you explain to some degree, how can you use it?

A - There are several lines of attack to the problem of using high Fe/Al ore for fertilizer production.

1. Some nitrophosphate processes are not seriously affected by high Fe/al impurities, and the product containing iron and aluminium phosphate, if precipitated in amorphous form, is a satisfactory fertilizer.

2. Partial purification by solvent extraction can be used to remove iron and aluminium phosphate from wet process acid.
3. Certain thermal treatments of some kinds of phosphate ore can render iron and aluminium insoluble in acid.
4. Some iron and aluminium compounds found in ores are relatively insoluble, so the calcium phosphate can be preferentially extracted by using mild extraction conditions (e.g. a deficiency of H_2SO_4 and moderate temperature).
5. The firm Superfos (Denmark) is developing a nitrophosphate process in which iron and aluminium (as well as calcium) is removed by iron exchange
6. TVA is developing a process in which low-grade phosphate rock is extracted by a mixture of acetone, water, and SO_2 . About 95 percent of the P_2O_5 , but only 50 percent of the Fe and 5 percent of the Al is extracted.

Q - Mr. S.B. PARIKH (Gujarat State Fertilisers Co, India)

Can you avoid sulfide formation during calcination of high organic rock? Sulfides present environmental problem in phos-acid plants.

A - Sulfide formation during calcination of rock containing organic matter can be avoided to some extent, by maintaining an oxidizing atmosphere during calcination. In fact, sulfides present in some phosphate rocks can be at least partially oxidized by calcination. Sulfide formation during calcination can occur due to localized reducing conditions which may be caused by poor air and fuel distribution or by poor contact of the oxidizing atmosphere with the ore.

Q - Mr. S.B. PARIKH

Can IFDC take up full-hedged program for identifying and standardising new rock falling in the category of low grade mentioned in the paper, which would include establishing the optimum operating parameters?

A - IFDC is a young organization and does not have in-house facilities for complete study of a new low-grade phosphate ore. However, IFDC has contractual relations with several other organizations including TVA, and will undertake a full evaluation of the best use of a phosphate ore including mineralogical and chemical characterization, beneficiation studies, and processing into fertilizer by various means. The study may include identification of optimum or near-optimum parameters after selection of the most suitable process. IFDC is expanding its staff and adding laboratory and pilot-plant facilities so more of this type of work can be done directly by IFDC.

Q - Please elaborate a method water washing and drying rock containing high chlorides.

A - The filter for washing phosphate rock to remove chlorides which was mentioned in the paper is a new type of filter resembling a rotary table filter with scroll discharge. The filter medium is microperforated stainless steel plate; there is no filter cloth. The phosphate

rock is slurried with wash water, settled to remove excess water and the thickened slurry is distributed on the table. The water is removed by vacuum, after which the rock is washed on the filter by fresh water sprays. After dewatering, the rock is removed by a screw discharge and the metal plate is washed to remove any particles lodged in the perforations. Advantages claimed are high capacity, low losses of rock, and minimization of water use. After washing, the rock may still contain 15 percent water; it may be dried by conventional means, or used without drying. If grinding is necessary, wet grinding may be appropriate.

TA/76/17 : Processing of standard rock, other rocks and rock blends in a same phosphoric acid plant by S.B. PARIKH, Gujarat State Fertilizer Co. Ltd., India (Rapporteur W.E. DUMOIS, ERT, Spain)

Q - Mr. D.W. LEYSHON (Jacobs Engineering, USA)

What are the units for defoamer consumption for table 9, p 303?

A - Mr. S.B. PARIKH

Units are Kgs per Metric Tonne of P_2O_5 produced.

Q - Mr. T.P. HIGNETT (IFDC, USA)

I question whether it would really be uneconomical to build a plant that could efficiently process all of the phosphate rocks usually encountered in commerce.

Has Mr Parikh any estimates on the cost of such plant? If so, would the cost really exceed benefit?

A - Mr. S.B. PARIKH

This is indeed a crucial question concerning phosphoric acid manufacturer as well as plant designer. Although there are many plants all over the world which use number of different rocks, unfortunately there is none which is really designed for all; and hence the economy under question is always a matter of estimate. Again the ultimate economy will depend upon the prevailing price conditions and hence will vary from country to country. Such detailed estimate of plant cost is basically a design problem and as GSFC is only a manufacturing concern I do not have any such estimate.

TA/76/18 The Veba phosphoric acid process by D. KURANDT, Veba Chemie, Germany (Rapporteur P. BECKER, Duetag, France)

The discussion which followed Dr. KURANDT's paper gave the possibility of enlarging the views on the potentials and characteristics of the special VEBA-CHEMIE process.

Dr KURANDT gave the following answers to questions from various speakers.

1- INDUSTRIAL ACHIEVEMENTS

Q - Messrs P.A. VENKOVSKY (E.I.M., Brazil) & A. KABIL (Donau Chemie, Austria)

A - One 100 t/d unit is operating at EMBSSEN, 60 km South East of HAMBOURG. It is equipped with a 9 m² Giorgini filter and has a reaction volume of 120 m³.

2- INFLUENCE OF THE RAW MATERIAL COMPOSITION

a - Organic substances

Q - Mr. A.B. PHILLIPS (TVA, USA)

A - The presence of organic substances in the rock affects nitric acid losses. However, by adjusting temperature, these losses can be reduced through slower oxidation reactions. Thus, in the case of uncalcined Florida rock, total N losses are estimated to 3 kg/t P₂O₅.

b - Phosphates from sedimentary origin

Q - Mr. E. JORGENSEN (Superfos, Denmark)

A - Phosphates from sedimentary origin are characterized by their tendency to foaming during reaction through release of CO₂ resulting from the presence of organic substances. This is also true for the VEBA process.

The foam problem is related to the area available in the reactor. Since the latter is smaller in the VEBA process, the foam layer tends to increase. However antifoaming agents are efficient likewise in that process and, thus, there is no problem.

c - Phosphates high in chlorine

Q - Mr. A. KABIL (Donau Chemie, Austria)

A - No test has been conducted with such products.

3- GENERAL CHARACTERISTICS OF THE PROCESS

a- Dual utilization, dihydrate-VEBA

Q - Mr. O. JENSSEN (Superfos, Denmark)

A - In the case of an alternate utilisation Dihydrate-VEBA, the addition of a second reaction system is recommended. One reactor should be in stainless steel for the VEBA process, and the other can be made of conventional materials for the dihydrate.

The other parts of the plant, i.e. the feed-measurements, filtration, cooling, can be common to both systems.

Since a stainless steel reactor is fairly cheap, and, in view of the high reaction capacity of the VEBA process, the cost is relatively less.

b- Nitrogen oxide emissions

Q - Mr. A.B. PHILLIPS

A - The emission problems of nitrous gases exist in all nitric acid reactions. However, in the VEBA process, these emissions are less, since the nitric acid concentration is lower.

Q - Mr. N. LAGERHOLM (Supra, Sweden)

A - In addition, the amount of N indicated, 2 kg nitric acid/t P_2O_5 , is not released in the atmosphere. With Kola phosphate for instance, N is lost in the form of HNO_3 and not NO_2 . About 1 kg N- HNO_3 remains in the gypsum and 1 kg in the liquid effluents. In the case of sedimentary rock, NO_2 can evolve as in any reaction between nitric acid and phosphates.4- MATERIALS OF CONSTRUCTION

Q - Messrs A.B. PHILLIPS & N. LAGERHOLM

A - The reactor is made of stainless steel - Type: 1.4435

Cr	16.5	- 18.5%
Ni	13.0	- 15.0%
Mo		2.0%
Si		1.0%
C		0.03%

The rate of corrosion depends on the temperature:

at 80°C	0.2 mm/yr
85°C	0.4 mm/yr
90°C	0.8 mm/yr

Agitations and tubes are also of stainless steel

Q - Mr. N. KOLMEIJER (Windmill Holland, Netherlands)

A - Rubber lining is not recommended, since rubber would slowly be attacked by nitric acid. Stainless steel, on the other hand, is little corroded by the presence of nitric acid.

The Giorgini filter is lined with special rubber, resistant to nitric acid. However this is not imperative, since there is no permanent contact between nitric acid and rubber.

In general, no abrasion was found in the reaction system except for a few types of pumps which, after replacement, proved satisfactory.

5- TREATMENT OF CALCIUM SULPHATE

Q - Messrs P. MORAILLON (Gesa, France) & A. KABIL (Donau Chemie, Austria)

A - The hemihydrate discharged is treated with lime to accelerate gypsum recrystallization. The water contained in the hemihydrate is then fixed by crystallization so that the product formed is dried.

At EBMSSEN gypsum is dehydrated in a kiln to produce plaster (for wetting or moulding). It can also be used in the cement industry as setting regulator.

VEBA-CHEMIE has no experience in the production of plaster board. However tests have been made which showed that this production is indeed possible.

The decision to produce plaster is merely commercial since, at present, it would be impossible to sell 130,000 t/yr plaster boards in Northern Germany.

TA/76/19 Performance and operation of the new Nissan phosphoric acid process plant by M. MIYAMOTO, Nissan Chemicals, Japan (Rapporteur P. BECKER, DUETAG, France)

Influence of origin and composition of phosphate rock

Q - Kola phosphate - Messrs M. QUINTON (Fisons Ltd, U.K.) & R. BARUT (Heurtey Industries; France)

A - There is no problem for using Kola rock. It was found that the rate of hydration of hemihydrate is lower than in the case of other rocks.

Q - 68 BPL rock - Messrs A.B. PHILLIPS (TVA, USA) & M. M'GAIEETH (SIAPE, Tunisia)

A - 68 Florida rock has been used and Nissan continues its tests in order to use still lower grade rocks.

Q - Influence of sulphuric concentration - N. KOLMEIJER, Windmill Holland, Netherlands

A - 67% H_2SO_4 sulphuric acid cannot be used without affecting phosphoric acid concentration. In the paper we indicate the possibility of using smelter acid.

Q - Limits of concentration of product acid - M.L. PARKER (Fisons Ltd, UK)

A - Usually Nissan guarantees 45% P_2O_5 but concentrations of up to 48% have been achieved.

Process

Q - Concentration of hydration tank in relation to hemihydrate filtration. N. KOLMEIJER

A - The P_2O_5 content in the hydration (or recrystallization) tanks is about 15-20% according to operational conditions. In practice it is not necessary to have a second washing on the dihydrate filter.

Q - Fluorine recovery - M. QUINTON

A - Fluorine is mainly recovered from off gases of the hemihydrate sector through scrubbers. Regular controls did not show any substantial scaling in spite of F/SiO₂ ratios mentioned in the question put by Mr. PARKER

Equipment

Q - Filters - Types and size - M. BARLOY (Lebanon Chemicals, Lebanon),
N. KOLMEIJER, R. MONALDI (Montedison, Italy)

A - Nissan uses tilting pan and belt filters.

The good cleaning of filter cloths is an essential factor in the choice of filters.

Filter size or surface area cannot be explained here. However orders of magnitude are 3-4 t/d P_2O_5/m^2 for hemihydrate and 6-8 t for dihydrate.

There is no recrystallization in the vacuum box of the hemihydrate filter and in the pipes of that filter. However its construction takes that possibility into account.

Q - Agitators for hemihydrate reactors - R. MONALDI

A - Turbine type pallet agitators are used. Their power consumption is about 1 KWH/m³.

Q - Heat exchangers

A - Tubular heat exchangers work well, without scaling problems of the acid circuit in which they are included.

Process economics

Q - Compared to dihydrate: investments and production.

Convertibility of the dihydrate process - S.B. PARIKH (Gujarat State Fertilizers Co. India)

A - Information on that subject were given in the paper by NISSAN at the ANDA/ISMA Symposium, Sao Paulo, April 1975. The conversion of a conventional dihydrate unit into a Nissan unit is possible, but the investment cost is not generally applicable, but each case must be considered separately.

Question put by Mr. M'GAIETH to the three authors of papers dealing with phosphoric acid.

The processes presented use preferably high grade phosphate rocks, which seems contradictory to the present trends of the phosphate rock market. What would be the performances with low grade phosphate rock?

Comments made by the rapporteur, under his own responsibility in addition to the partial answers given by the various authors:

In the processes producing highly concentrated acid much higher recycling of already filtered P_2O_5 would be necessary to keep an adequate liquid/solid ratio in the reactor according to the concentration desired. In addition the recycling also depends on the P_2O_5/CaO ratio of the rock used, P_2O_5 making the liquid phase, CaO the solid phase.

In other words, a low grade rock would still increase the recycle rate of P_2O_5 in the unit. This could be a limiting factor for lower grade rocks. In that case the phosacid should be filtered 4 times with the risk of heavy losses associated with a badly adjusted or inefficient filtration (see table).

Phosphate rock	tons P_2O_5 of the acid getting through the filter per ton P_2O_5 introduced in the unit	
	Dihydrate Acid process 29%	Hemihydrate acid process 45%
Low grade rock 28% P_2O_5 49% CaO	2.7	4.1
High grade rock 37% P_2O_5 51% CaO	2.1	3.2

TA/76/20 Full scale operating experience of the Fisons HDC phosphoric acid process by J.P. HILL, Fisons Ltd. U.K. (Rapporteur P. BECKER, DUETAG, France)

After Mr. Robinson's presentation, the questions put to him enabled the author to give the following information about HDH Fisons process.

1) Influence of the origin and composition of raw materials

- Q - Mr. A.B. PHILLIPS (TVA, USA), Mr. D.W. LEYSHON (Jacobs Engineering, USA), Mr. M. M'GAIETH (SIAPE, Tunisia)
- A - In general it can be stated that the HDH process is more suitable to high grade than to low grade phosphates. However in a hemihydrate plant, tests were carried out with uncalcined 65 Florida rock. On the basis of the results of this test, it is expected that this phosphate could also be used in the HDH process. Efficiencies similar to those achieved with Morocco rock could be reached, but filtrability would be reduced owing to the presence of organic matter.

The Trepca plant was designed to use Khouribga 75/77 rock (Morocco). However it also processed Youssoufia and Khouribga 72 rocks (Morocco). Togo rock has also been tested in the Windmill hemihydrate plant for 6 years. All the results with these phosphates agree with those obtained in our pilot plant from which we can expect a similar situation after pilot tests conducted with Florida rock.

Low grade phosphates often have a high organic matter content, which, as also mentioned, affects filtrability. We can get the same efficiency provided we operate at lower capacities.

We also used calcined North Carolina rock and achieved the same P_2O_5 efficiency as with Khouribga rock. Half the filtration capacity was reached when filtering hemihydrate, as compared to Khouribga rock.

Kola phosphate gives a very stable hemihydrate which rehydrates slowly. We do not recommend it for the HDH process.

With 75/77 Khouribga rocks no antifoaming agent is used.

2) Crystallization - Gypsum quality

Q - Mr. P.A. VENKOVSKI (EIM, Brazil), Mr. A.B. PHILLIPS

A - a) Possible formation of anhydrite

No anhydrite forms in the HDH process, except when the plant is stopped. In normal operation, it never happened. In 6 years' production at Windmill, there was never any anhydrite formation.

At Treпча, there was an incident during a several weeks' halt which had been decided for mechanical reasons. There was a double effect due to high temperature and high P_2O_5 concentration, which could not be adjusted in time. This incident was not repeated during the stops which followed the 12 months' production.

b) Composition of gypsum crystals

The main difference in gypsum composition from the HDH and the dihydrate processes stems from the proportion: aluminium, fluorine, iron. In the case of Morocco rock, the following composition can be given:

in % of phosphate constituents

	HDH Process		Dihydrate process	
	Product acid	Gypsum	Product acid	Gypsum
Al_2O_3	18-26	74-82	55-60	40-45
F	10-15	23-28	6-8	33-35
Fe_2O_3	81-83	17-19	90-94	6-10

The fluorine content of gypsum in the HDH process is lower than in the dihydrate process. The same applies to P_2O_5 . The product acid in the HDH process contains less iron, aluminium, sulphates and solids.

3) Fluorine recovery

Q - Mr. J.W. BAYNHAM (SAI, U.K.)

A - The HDH and hemihydrate processes recover fluorine from the reaction slurry when the latter is cooled. In the dihydrate process, most of the fluorine is recovered during acid concentration in the evaporators. This is where the biggest difference is.

Owing to the P_2O_5 concentration, the temperature and the amount of water evaporated from the slurry, the SiO_2/F in the gases discharged is higher in the hemihydrate process. This raised problems with the hemihydrate process resulting from SiO_2 scaling.

The SiO_2/F can be reduced by adjusting the concentration of the product acid to 50% P_2O_5 or more. However, in the single stage filtration process, it reduces the P_2O_5 efficiency, which is a must. At the Windmill plant, the SiO_2/F is adjusted by mixing recovered H_2SiF_6 coming from other units. On the other hand, in the HDH process, the efficiency is not affected by the strong acid concentration.

In Trepca, our fluorine recovery unit is not working full capacity for various reasons, but mainly because it is not yet possible to use the recovered fluorine.

However, in Trepca, fluorine recovery has worked long periods and achieved the anticipated efficiencies. There is no silica scaling problem and we hope that it will be confirmed by the future operation.

4) Equipment

Choice of filter type

- Mr BARLOY (Lebanon Chemicals, Lebanon)
- An essential factor when selecting the filter is an efficient cloth washing after the filtration cycle. Up till now our experience relates to a rotary tilting pan filter, but no reason should hamper a belt filter or a table filter.

In comparison, belt filters are limited in area and operate only with two washings while three are necessary, and they usually work with a lower vacuum. However, the belt filter has two advantages: its cloth is washed better and there is no mechanical loss due to the pans. These two advantages are more important in the case of the hemihydrate process than in the case of the dihydrate process.

3rd Working Session : NPK fertilisers

TA/76/11 Slurry ammoniation in complex fertilisers production. A new type of high efficiency ammoniator by I. MINI, R. MONALDI, Montedison SpA, Italy. (Rapporteur R. LOSTE, S.A. Cros, Spain)

Q - Several participants: Messrs J.D. CRERAR (Fisons Ltd, U.K.), A.B. PHILLIPS (T.V.A., U.S.A.), J.L. TORAL (S.A. Cros, Spain), etc.. asked questions concerning the ammoniation system.

A - Mr. I. MINI

In our ammonia absorption system the slurry is pumped into a pipe where NH_3 and fresh H_3PO_4 are also fed and the neutralization takes place. The pipe pours the resulting slurry into a flash tank, below its liquid level, thus avoiding steam formation in the pipe. The capacity of the flash evaporator is less than $1 \text{ m}^3/\text{t NH}_3$ absorbed.

The power consumption of the recirculation pump depends on the viscosity and the height and length of the upward pipe. Usually, absorbing $5 \text{ t NH}_3/\text{hr}$ the power is in the range of 100 KW.

Q - Mr. J. FRÖCHEN (Cofaz, France)

The author has emphasized the importance of having lower temperature inside the drum granulator in order to decrease recycle. Our experience is, on the contrary, the higher the temperature the lower the recycle, so we try to inject NH_3 directly into the product during granulation.

A - Mr. I. MINI

Your remark is perfectly sound. But I think it is not possible to generalize. Each case will have an adequate treatment and looking to the changes of solubility due to temperature, our process can satisfy both requirements as well.

Q - Mr. N. KOLMEIJER (Windmill, Holland)

Your reactor is very similar to the neutralizer used by Uhde for the manufacture of ammonium nitrate solution, where the high circulation rate controls the temperature gradients to avoid the process steam generation at the spot where ammonia is introduced. I think your novelty is that you apply it for N-P fluids.

A - Mr. I. MINI

In Uhde as well as in other processes the slurry is discharged above the slurry level. In our process the slurry enters in the flash evaporator below the liquid level. So it is to ensure that the upward tube is always full only with slurry and without any process steam.

Q - Mr. P. MORAILLON (Générale des Engrais S.A., France)

The author showed a very interesting set of experimental results using a pipe reactor with a forced recycle by pump. Has Montedison done any test with natural recirculation or even without recirculation ?

A - Mr. I. MINI

The viscosity obliges to force the recirculation.

Q - Mr. K.L. PARKS (Agrico, U.S.A.)

Could your reactor be considered a "Tee" reactor with recycle ?

A - Mr. I. MINI

Yes.

Q - Mr. K.D. SHAH (ICI, U.K.)

Referring to the High Efficiency NH_3 Absorber described in the paper, I would like to ask about the extent of temperature rise achieved in the NH_3 absorption zone by the reaction heat and the pressure required to maintain total liquid phase.

A - Mr. I. MINI

The extent of temperature rise is between 5 and 30°C. The variation depends on:

- the quantity of absorbed ammonia, and chiefly the specific quantity of evaporated water related to absorbed ammonia.
- the slurry flow rate which depends on the height of the apparatus

The pressure is bound to the above mentioned height. The possibility to maintain total liquid phase comes from a relation between height available, specific weight and specific heat of the slurry, slurry flow rate and viscosity of developed water vapor, characteristics of the pumps.

R - Mr. G. SIEBERT (BASF, Germany)

BASF-Ludwigshafen has made, since 1970/71 several works in the same way as Montedison concerning the phosphoric and phosphoric/nitric acids ammoniation. The BASF process, like the Montedison one, makes the ammoniation separately from the spontaneous vaporization, due to the heat of neutralization. However, BASF has further steps to complete the evaporation while the ammoniation is also completely achieved, so in the granulator drum no excess of NH_3 appears. There are two production lines working with this BASF process in Ludwigshafen. The Ludwigshafen trials are coherent with the Montedison works.

A - Mr. I. MINI

We take note about the remarks by Dr. G. Siebert. As far as the drum ammoniation is concerned, this appeared not to be usually the best way of conducting plant. For this reason we usually choose the best ratio between NH_3 in slurry ammoniator and NH_3 in drum-ammoniator. Regarding the separation of NH_3 absorption from water evaporation we remember the Fauser reactor for ammonium nitrate (B. Patent n° 625004) specimens of which have been operating since 1938.

TA/76/12 Direct production of granulated superphosphates and PK-compounds from sulphuric acid, phosphoric acid, rock phosphate and potash by A. SINTE MAARTENSDIJK, UKF, Netherlands, (Rapporteur: F.W. BOOS, Gewerkschaft Victor, Germany).

Q - Mr. A.B. PHILLIPS (T.V.A., U.S.A.)

1. Is there an evolution of fluorine or chlorine in the granulation stage and, if so, how is it recovered?
2. Is there a corrosion of the shell of the drum granulator, or of the shell of the dryer?

A - 1. There is evolution of some fluorine during the granulation stage, however, this is small as the greater part of fluorine evolves during the entire granulation-, drying- and cooling-operation approximately 1% originates from the Granulator. In the case of Chlorine, some hydrochloric acid is involved in the granulation-process. This amount depends very much on the formula of the product produced. In the case for instance 0-7-30 approximately 1.5% of the total quantity of Cl is converted into HCl. Of this amount 2% escapes during granulation and 98% during drying and cooling. As shown in the flowsheet, the F- and HCl-gases from the granulator are passed through a separate scrubber.

A - 2. There is some corrosion of the shell of the granulation drum. Especially at the inlet-end of the drum, where steam and water are introduced. This can, however, easily be solved by applying a suitable lining at this particular part of the drum. The remainder of the m.s. lining of the granulator has not shown much corrosion since the plant went into operation about two years ago. Especially as the plant started up on an extended production-run of superphosphate the granulator received a more or less protective inside coating of superphosphate. We have not established any significant corrosion of the dryer-shell so far.

Q - Mr. N. LAGERHOLM (Supra, Sweden)

1. Referring to the Section of fume and dust extraction, I should like to ask what is done with the water from the scrubbers for the gases from the granulator, dryer, cooler, etc...? This water presumably contains rather more HCl, fluorine and perhaps more phosphorus than in conventional processes and can therefore probably not be simply drained.

2. Mr Maartensdijk states that products produced in the process are of quality superior to that of products produced by conventional methods. Would he care to specify in what respect?

- A - 1. In the location where we built this plant we were in the fortunate position that we may discharge the effluent from the scrubber, which however, must meet high standards as required by the Authorities. pH-correction of the effluent is necessary and, consequently, neutralisation to a pH of over 5 is required before discharging the effluent.
2. Because granulation in this process is much better than when operating according to conventional methods, the granules are more uniform, have a better shape, are smoother (less recycle, less over-size etc...) and have a hardness at least equal to that of conventional products.

Q - Mr. T. LOEWY (Fertilizers & Chemicals, Israel)

1. We note a coating drum on the flowsheet. Which products do you coat?
2. We note from f/s that the superphosphate and potash are not pre-mixed prior to granulator. Can the author explain considerations for eliminating premixer and whether 100% homogenous product is obtained?
3. What is the normal hour capacity of the plant?
4. What is the recycle ratio (+tph product/tph throughput) when granulating superphosphate? When granulating 0-10-20?

A - 1. Products like 0-10-20 and 0-7-30 are coated when they have to be stored for longer periods.

2. Potash is fed on the recycle-conveyor and both are together with the fresh superphosphate fed into the raw-materials bucket elevator. This elevator already gives a certain degree of mixing which continues in the granulation-drum. We have found that no additional mixer for the raw materials is necessary and the standard deviation of the analysis of spot-samples confirmed that this mixing is quite sufficient.

3. The hour capacity depends on the product-formulation and differs for T.S.P., S.S.P., 0-10-20 and 0-7-30. Generally, we can say that the normal capacity varies from 20 to 35 t.p.h.

4. Recycle-ratios are as shown in table 1 on page 206. So for instance for S.S.P. the recycle ratio (Recycle : Product) = 0.63 : 1 or (product : throughput) = 1 : 1.63.

Q - Mr. I. MINI (Montedison SpA, Italy)

There is a difference in P-yield among the different types of fertilizers

1. What is the reason for that?
2. What is the yield if considering the citrate-soluble P?

A - 1. I assume that Mr. Mini refers to the figures in Table 2 on p. 207. The figures in this table are taken at random from different production runs. The difference in water-soluble P-yield is mainly caused by different degrees of acidulation of the rock-phosphate. This can be checked by the figures free phosphoric acid in the corresponding columns. In the case of 0-7-30 for instance, it is clear that, compared with 0-10-20, the rock phosphate has been underacidulated.

2. When determining the citrate-soluble P-content it is of importance which method is applied; the citrate-solubility for instance can be determined in alkaline or neutral ammonium citrate, both methods giving different results. As for the products produced in this plant only water-soluble P is of commercial value. We usually do not determine the citrate-solubility. We have, however, at times done this and found recoveries of 95-99%.

Q - Mr S.L. PENG (C.R.A., Brazil):

What is the retention time in the Broadfield den?

A - As a rule the retention time in the Broadfield den is kept at a maximum, in order to let chemical reactions proceed as far as possible before granulation. In practice the retention-time varies from about 25-45 minutes.

Q - Mr. J.D. CRERAR (Fisons Ltd, U.K.)

1. I have two questions on corrosion aspects:

- a) Polypropylene ducting and a reinforced dryer are mentioned as protection against HCl-attack; what material is used for the dryer fan and with what results?
 - b) What is the maximum temperature to which UKF has had good experience with polypropylene?
2. Can UKF tell us where it operates the process described and on what scale?

A - 1a. The dryer fan is made of m.s. Because it is located after the cyclones and before the wet scrubber, where the gases are always well above the dew point, we have had no problems of corrosion of this fan.

1b. The maximum temperature for polypropylene, guaranteed by the supplier was 110°C, however, we normally operated at temperatures from 75-90°C with good results.

2. The plant described in this paper is located in Ireland and in operation for about two years.

Q - Mr. C. KELETI (UNIDO, Austria)

1. Low recycle ratio was mentioned. What is the average recycle ratio and does it vary as per product fabricated?
2. What recycle ratio do you adopt for design-purposes?

A - 1. Recycle ratios are given for some different products as shown in table I at p. 206 and vary from 0.63:1 for single superphosphate to 1.25:1 for triple superphosphate. For 0-10-20 and 0-7-30, the recycle ratios are about the same, viz. 0.8:1.

2. For design-purposes we apply the figures as mentioned under 1.

Q - Mr. I.A. BROWNLIE (S.A.I., U.K.)

If the process is used for NPK production, will not the product cake, unless moisture is reduced to about 1%? In these circumstances will the conversion efficiency of the superphosphate not be reduced because superphosphate does not mature under these conditions?

A - We have produced a compound 5-5-10 from fresh superphosphate and ammonium sulphate. The product was dried to a moisture content of minimum 2% and, after applying a simple coating, stored for a long period of time. Under those conditions we experienced no caking of the product and no reduction of the conversion efficiency.

Q - Mr. J.T. HARTUNG (Superfos, Denmark)

1. Direct flow to a weigh-belt from the mill of the rock phosphate could give fluctuations in the weight. There is no hopper in between to avoid or reduce these fluctuations. Is this to avoid segregation in fineness?

2. The specification of 90-98% through 0.1 mm for the rock phosphate is rather fine. What is the power consumption per ton of ground rock phosphate?

3. One of the expected draw backs is this process if the magnitude of evolution of hydrochloric acid. Can you give us figures for the evolution per ton of PK-granulates?

4. With the rather high water content in the final products we would like to know if the handling and storing qualities of the products are quite satisfactory. Or is the choice of final water content in the PK product a sort of compromise to avoid excessive hydrochloric acid formation?

5. What is your experience with repair-costs due to corrosion?

A - 1. As I mentioned in my introduction we have an accurate control system on our grinding mills and as result of this the variance in output of the mill, over extended periods of time, is usually within 2%. Omission of a storage hopper avoids segregation of the ground rock phosphate and has the added advantages of a constant temperature of the rock and better mixing due to aeration.

2. The power consumption per ton of ground rock is of the order of about 25 kwh/t.

3. During the process approximately 1.5% of the total quantity of Cl⁻ evolves as hydrochloric acid.

4. With a moisture content of 4-6% in the finished products the handling and storing quality is very good. When storing for extended periods of time coating is applied for PK products to eliminate caking. We chose this moisture content in order to maintain high water soluble P recoveries and at the same time avoid excessive hydrochloric acid evolution.

5. As a result of the fact that we paid much attention to selecting suitable materials of construction, and a wide application of plastic materials we found that our repair costs due to corrosion is not excessive but even somewhat lower than anticipated.

Q - Mr. A.M. VERDASCA (C.U.F., Portugal)

1. In your plant, did you experiment the production of NPK fertilisers involving the introduction of ammonia in the granulator taking advantage of the residual acidity of superphosphate or even by adding other nitrogen feedstocks? What results did you get?

2. You think that your process is applicable without the use of a Broadfield den, by feeding the slurry, after more thorough mixing, directly into the granulator?

On that basis, what is the degradation into insoluble pyrophosphates which could be considered in the drying, and do you believe that P_2O_5 will still solubilize during curing in fertilisers with a final moisture of about 5%?

A - 1. Our aim when introducing this process was to produce products with a maximum of water soluble P_2O_5 . For this reason we have not introduced ammonia in our system, because, as you know, ammoniation of superphosphate reduces the water solubility to a large extent. As I mentioned earlier we have used solid ammonium sulphate as a raw-material for NPK compounds with good results.

2. One of the principles we adopted in this process was to allow chemical reactions between acid and rock phosphate to progress as far as possible before addition KCl and granulation, in order to maintain water soluble P_2O_5 and reduce HCl formation. I expect this would not be possible when introducing the slurry from the mixer directly into the granulator.

TA/76/13 The conversion of calcium nitrate originating in a nitrophosphate plant with a view to improving the efficiency, as well as a survey of the possible applications of the products by G. LANGHANS, Hoechst AG, B. BIENIOK, Friedrich Uhde GmbH, Germany (Rapporteur: F.W. BOOS, Gewerkschaft Victor, Germany)

Q - Mr. I. MINI (Montedison SpA, Italy)

1. Why was apatite preferred to Dicalcium phosphate as P-carrier-precipitate?

2. Is there any possibility of scaling on the cooling coils? (in the reactor fig. 4).

3. What is the scope of the coils? To avoid H_2O evaporation?

4. Why is NH_3 sent in at many points?
Does the pH variate along the column?

A - 1. As we can see from fig. 2, test A, which produced dicalcium phosphate, lasted 100 min. It was then possible to let the hydrolysis of fluosilicate and the precipitation of phosphate take place one

after the other. Through continuous neutralization the two reactions take place simultaneously and produce apatite. In reaction conditions which must be followed to obtain a precipitate with good filtration properties, dicalcium phosphate cannot form.

2. Yes, there is scaling on the reactor. We remove the calcium carbonate scaling after one week with 60% nitric acid. The resulting solution is then slowly fed into the reactor. Cleaning the reactor means stopping the plant for 8-10 hours. If it is impossible, because of the retention of calcium nitrate, which we can do, or, for other reasons, because the operation cannot be interrupted, it is advisable to have a second reactor.

3. In the tests which, formerly, Dr. Schäfer conducted in his laboratory, it was found that one must keep quite a constant temperature in the reactor. In order to remove the reaction heat, the reactor is equipped with three cooling systems. It is not possible to cool the steam, since ammonia losses would be too high.

4. Yes, you are right. At the top of the reactor the pH was lower than at the bottom, where the slurry was discharged. When the reactor is operated that way, the calcium carbonate particles grow to the size necessary to produce calcium ammonium nitrate.

Q - Mr. O. KJOEHL (Norsk Hydro, Norway)

1. What are the sizes of crystals formed during the neutralization with NH_3 ?

2. Which rock phosphates have been used, and have any of these given special problems with regard to filterability?

A - 1. The apatite particles are smaller than 0.02 mm.

2. We process phosphates from Florida and Africa. There is only one phosphate, which I cannot mention here, for which we had difficulties associated with apatite filtration. These difficulties could be overcome by processing a mixture of this phosphate with others. With Kola phosphate, which we processed on one occasion, we did not experience any difficulty.

Q - Mr A. SLETHOLT (Norsk Hydro, Norway)

1. What type of cloth is used on the rotary drum filters for calcium carbonate?

2. Could you indicate the lifetime of the filtercloth of the above mentioned filters, and the need for maintenance of the cloth between replacements?

A - 1. For the filtration of calcium carbonate we use polypropylene filter cloths.

2. The filter cloths have a life time of about 6 months. Only in exceptional cases, we must wash the cloth with nitric acid.

Q - Mr. O.H. LIE (Norsk Hydro, Norway)

1. The presence of occluded NH_4NO_3 in the CaCO_3 , does it cause any problems in the cement production?

A - We have indicated to the cement industry that the lime contains occluded nitrogen compounds. We have never heard of problems resulting from that. We must, however, state that the nitrogen compounds are destroyed by the high temperatures during the production of cement-clinker.

TA/76/14 Economic and technical aspects in some differential NPK processes by M.AUTTI, M. LOIKKANEN and P. SUPPANEN, Kemira Oy, Finland (Rapporteur F.W. BOOS, Gewerkschaft Victor, Germany)

Q - Mr. M.G. GAURON (Cofaz, France)

How can you explain the lower watersolubility of P_2O_5 in process 2, in which only phosphoric acid is used as P_2O_5 source (Table 4, total P_2O_5 20%, watersoluble P_2O_5 16.2%).

A - Mr. P. SUPPANEN

In process 2 we use unfiltered phosphoric-acid-slurry from the phosphoric acid plant and this is the reason for the decreased watersolubility of P_2O_5 in the product.

Q - Dr. F.J. KAVANAGH (N.E.T., Ireland)

It is interesting that you advocate use of fuel oil and talc without use of amine. Which type of fuel oil do you use?

A - Formerly we used oil-amine and talc for anticaking, but recently we have changed the system and now we are using heavy fuel-oil and talc. The fuel-oil is the same as the one we use in our burner. With this fuel-oil-talc anticaking method, we have got very good results. As you know, climatic conditions in Finland are quite different in different seasons. In the winter it is very cold and in summertime it is warm and with this anticaking system we have at the moment no problems with NPK-caking.

Q - Dr. R. van HARDEVELD (UKF, Netherlands)

How do you measure the % attrition of your granules. How do you standardize this method and is there any relation between your attrition-index and the properties of your product in regard to dust formation and so on.

A - Our laboratory has developed our own method to measure the attrition of granules. This measurement is performed under standard conditions and the attrition index gives us an idea of the tendency to dust formation during drying, cooling and generally in product handling. With this index we can compare different granules in their tendency to form dust.

Q - Mr. J.D. CRERAR (Fisons Ltd, U.K.)

1. In these days of increasing environmental concern, one has to look at alternative methods of cleaning gases. I would like the authors to expand a little on their experience with bag filters on cooler gases.

- a) What type of bag is used?
- b) What bag life is experienced?
- c) Are cyclones retained prior to bag filters?
- d) Is any dust deposited in the air-heater of the drier?

2. Would the authors confirm that the recycle ratios of processes 1 and 3 are 6:1 and 2,5:1 expressed conventionally as fines/production rather than the reverse (1:6 and 1:2,5) as given in the paper.

A - 1. We have used bag filter on cooler gases in our newest fertilizer plant with good success. The filter material has been polyester. We have no cyclone at all for cooler gases. Cleaned cooler gas has been used in drying as dilution air and this gas recycling has decreased oil consumption in drying. We are just planning to use this system in our other fertilizer plants. There has not been any dust deposit in the heater of the drying system.

2. The recycle ratios are 6:1 and 2,5:1 expressed as recycle/product.

Q - Mr. P. ROLFSEN (Norsk Hydro, Norway)

Process 3 is the most economic one, but must have higher raw-material costs than the Odda process - which is its main advantage versus that process?

A - I cannot compare our processes with the ODDA-process because of different starting point and local conditions. In our company we have lots of sulphuric acid production and the price is moderate. For this reason we produce phosphoric acid for phosphoric raw material instead of using the nitrophosphate process. If we had cheap ammonia and nitric acid instead of sulphuric acid we would perhaps use the ODDA-process.

Q - Mr. H.F. KURANDT (Veba Chemie, Germany)

Why don't you use rock phosphate in process 2 to reduce the cost of raw materials as in process 3, but a phosphoric acid slurry?

A - Process 2 is designed for the use of phosphoric acid and there are only two reactors. If we want to use phosphate rocks as phosphoric raw material we need more reactors and at the moment we do not have these.

Q - Mr. N. LAGERHOLM (Supra, Sweden)

From table 4 on page 245, it appears that most of the water-insoluble P_2O_5 is present as precipitated apatite and not as dicalcium phosphate ($CaHPO_4$). Is this considered satisfactory from an agronomic point of view?

A - Unfortunately I do not know very much about these agronomic questions but this "precipitated apatite", mentioned in our paper, should be precipitated tricalcium phosphate and this has certain solubility and agronomic value.

TA/76/15 Low investment and optimisation in the production cost of an urea MAP-NPK fertiliser complex by F.G. MEMBRILLERA, J.L. THORAL and F. CODINA, S.A. Cros, Spain (Rapporteur R. LOSTE, S.A. Cros, Spain)

Q - Mr. B. BIENIOK (Friedrich Uhde, Germany)

What is the humidity at the outlet of the granulator and in the final product when using urea prills or urea solution in the production of 15-15-15?

A - Mr. F.G. MEMBRILLERA (S.A. Cros, Spain)

With urea prills, we work normally with a humidity in the outlet of granulator of about 2.5 - 3.0% and in the final product about 1.0%. With urea solution the humidity is a little higher but not so much, otherwise the tendency in the granulation is to oversize. What we do is to increase the recycle ratio to maintain 3.0 - 3.5% in the outlet of the granulator.

Q - Mr. I. MINI (Montedison SpA, Italy)

Are there any problems of scaling and erosion in the "T reactor"?

A - Mr. F.G. MEMBRILLERA

About scaling I can tell you that, due to the high velocity, we maintain in the "T reactor", the problem of scaling is completely unknown. We never stop the reactor to clean it.

About erosion yes, we have had in the past troubles in the outlet tube of the "T reactor" using 317-L or 316-L. We have avoided the corrosion problems and, about erosion, our experience is that one exit tube can be in operation during 3,000-4,000 hours and the cost of this tube is negligible compared to the rest of the equipment.

Q - Mr. I. MINI (Montedison SpA, Italy)

What is the capacity of the DAP plant?

A - Mr. F.G. MEMBRILLERA

Our NPK unit is also able to produce DAP. The capacity of this unit is 120,000 T/yr of NPK grades. It is well known that the capacity is not the same for different grades but we can say that the production is 20 T/hour. In the case we are producing MAP the capacity according to the size of the final product can be between 14 - 20 T and for DAP 10 T/hr.

Q - Mr. R. MONALDI (Montedison SpA, Italy)

In the present situation working with a neutralization ratio 1.3 - 1.35 what is the consistency of the time losses to clean and scaling troubles?

A - Mr. F.G. MEMBRILLERA

In the beginning we had a lot of troubles with blockages mainly, but not at present due to the actual working pressure. The slurry is pushed out by the steam generated in the reaction. We know also now that it is very important to maintain a good control of the ammonia and the acid.

Knowing how to start up and shut down the reactor you avoid most of the potential troubles. Normally we do not clean the reactor but, when we do it, it can take 10 - 15 minutes. We have had two reactors in operation for nearly two years in the NPK unit in Malaga.

About scaling, we never have had any trouble at all. This is unknown to us.

Q - Mr. R. MONALDI

In the operating conditions of the CROS process, we see a neutralization ratio of 1.3 - 1.35 and I ask if there are difficulties in rising such ratio.

Q - Mr. F.G. MEMBRILLERA

No, there are no difficulties to rise the ratio to values such as 1.6 - 1.7 but, as normally the ammonia losses in the reactor increase, it is necessary to recover it in a scrubbing system. We think that up to date, it is possible to increase the ratio to 1.5 but we do not think it is of interest to increase it further.

Q - Mr. R. MONALDI

In the comparison of the classic DAP process and the CROS process, the main difference lies in the use of the "T reactor". We ask if there are other noticeable differences.

A - Mr. F.G. MEMBRILLERA

Yes, there are other differences indeed. The equipment used is more simple because there is only one scrubber and no pumping equipment at all to handle the slurry. Also, as a consequence of using the "T reactor", the recycle ratio is smaller and therefore the equipment is also smaller. I must tell you that the saving in fuel-oil due to the low humidity in the slurry is nearly ten times.

Q - Mr. G. DUMOIS (E.R.T., Spain)

If you use urea solution and 50% P_2O_5 phosphoric acid in your NPK granulation unit; what is the concentration of the urea solution and what is the temperature?

A - Mr. F.G. MEMBRILLERA

Well, we can use urea prills in our granulation unit as well as urea solution from our urea unit. Our urea unit is a once-through stripping plant, it means that the concentration of the urea solution in the outlet of the decomposition stage is as high as 85% w.w. At that time we did not have in the granulation unit the necessary equipment to make a more concentrated solution and for this reason we could not use the urea solution more than in grades such as 8-15-15 or 15-15-15.

Another question very important is that the concentration of phosphoric acid is not 50% but 52% and the water content about 14 - 15% w.w.

TA/76/21 Innovations in slurry process granulation plants by D.W. LEYSHON
Jacobs Engineering, USA, I.S. MANGAT, Humphreys & Glasgow, U.K.
(Rapporteur R. LOSTE, S.A. CROS, Spain)

Q - Mr. P.L. BALDWIN (Cremer & Warner, U.K.)

Can the author elaborate on the idea of automatic recycle control on p.385?

A - Mr. D.W. LEYSHON

Automatic recycle control is accomplished by measuring recycle by a weigh scale or elevator power sensing device and adjusting product take out to maintain recycle constant or at the desired level. This system is in operation in several plants.

Q - Mr. P.L. BALDWIN

How can the product screen feeder give the operator a running analysis of the fine fraction of the recycle?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

A rough indication of the percent of the material which is product size can be established if the product screen feeder is calibrated or if a weigh belt is used. This should allow an operator to establish whether this recycle is going finer or coarser at any moment rather than depending on visual grab sampling.

Q - Mr. I.A. BROWNLIE (Scottish Agricultural Industries Ltd, U.K.)

With reference to p. 371 "Granulation plant control" is it not an advantage to take product size material out as it is formed and is it not a disadvantage and waste of energy that in your process the product requires to be needless recycled in order to satisfy excess liquid phase?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

We do not believe operation at 2,5: 1 to 4,5: 1 recycle represents a significant quantity of power.

Q - Mr. J.D. CRERAR (Fisons Ltd, U.K.)

I think some of the advantages claimed are not peculiar to that process, for example: a) no raw material preparation, b) low stack losses, c) no H_2SO_4 use, are also features of the low recycle process.

A major disadvantage of the slurry process is the high recirculating solids loading which will limit plant capacity and consume a lot of power. What production rate is predicted for the 4 to 5 m diameter drier mentioned in Section VII?

A - Mr D.W. LEYSHON and Mr. I.S. MANGAT

Roughly speaking, we are talking about DAP capacities of 100 TPH and 125 T in 4 to 5 m diameter driers.

Q - Mr. J.D. CRERAR

The use of 42% phosphoric acid for the slurry process is claimed as an advantage over the MAP powder route which uses about 50% acid. Is not the water evaporation process producing 50% acid (i.e. phosphoric acid concentration unit) more efficient thermally than the dryer of fertilizer in a rotary drum?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

Yes, water evaporated in the dryer is less efficient thermally than water removed in a conventional evaporator but there are several other intermediate steps in going to MAP which are avoided. It is understood that the solid MAP based operation requires steam or water in the granulation step so that at least part of the water previously removed from the 50% P_2O_5 feed acid is reintroduced to the system and has to be taken out in the dryer.

R - Mr. N. KOLMEIJER (Windmill Holland, Netherlands)

I agree with you that the articles found in the literature emphasize too much the benefits of low recycle and that the authors often look at this as a goal in itself.

At Windmill we have experienced with both high and low recycle operation and we can confirm many of your statements about the relevant advantages of the high recycle process, such as easy drying and screening, better granule appearance and steadier output. The latter comes from the fact that the production rate is dictated by the water and heat balance rather than being dependent on the skill of the man who operates the granulator.

I believe one aspect has not been mentioned, namely that in extremely low recycle plants it is hardly possible to return scrubber effluents to the granulator because these will quickly spoil the water balance and thus affect the capacity.

I can confirm that in our low recycle plant we need about 20 min dryer-retention time in order to reduce the moisture content of our NPK s to a sufficiently low level.

Where I do not agree are your statements in the last paragraph on page 389 of the preprint. My objection is that you generalize on the physical and granulation properties of non-granular MAP.

IFFCO's experiment was done with a microprilled form of MAP, a type of material with which Windmill now have intensive experience, as we ourselves have been operating a plant producing MAP of such quality for 8 years. The material indeed shows too much caking tendency and its granulation properties are relatively poor.

If we use this material in our low recycle plant, because of low efficiency in granulation, we get much less output than one would at first sight anticipate on the basis of the water/heat balance.

On the other hand we know that PHOSAI which is a crystalline form of MAP does not cake at all and that it really granulates like SSP. It is our experience that when using this type of MAP the moisture level in the granulator is lower and the drier loading consequently less.

If we use this type of MAP in our plant, the output is much higher, as the good granulation efficiency allows us to gain the full benefit of the more favourable water balance.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

We have not enough experience in this particular point. It was only the opinion of IFFCO.

Q - Mr. R. LOSTE (S.A. Cros, Spain)

The pipe-reactor has made the same work as a conventional pre-neutralizer reaching the 1.4 ratio. What do you think about the difficulties to change a slurry of a conventional plant to a slurry based in T reactor operation?

A - Mr D.W. LEYSHON and Mr. I.S. MANGAT

There are not difficulties to install. But we think that in the cases of where it is necessary to continue ammoniation in the drum from 1.4 N/P to 1.9 due to low recycle and water content some problems can be found in the total NH_3 recovery. But we believe that T-reactor represents a potential advantage to improve the performance of NPK slurry based process as far as the recycle ratio is concerned.

Q - Mr. J. MASSART (UCB S.A., Belgium)

Which is, according your experience, the best way to control dust evolution from the dryer (and for cooler) drum, bag filters, cyclones or wet scrubbers? Or a combination of these means?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

The wet scrubbing, because of water balance. But bag collectors are gaining favour. In our opinion the future trend will go towards the use of dry collectors in the plant.

Q - Mr. J. MASSART

Which is the dust level permissible in your case?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

With wet scrubbers the dust is very low.

Q - Mr. A.B. PHILLIPS (TVA, U.S.A.)

Is there no identifiable urea when regular size urea is fed in the slurry process?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

Based on examination of product from one operating plant we have not found any identifiable urea in the product when regular size urea is fed to the plant. Hardness tests on product granules did not reveal any irregularities such as would be associated with localized concentration of urea.

Q - Mr. A.B. PHILLIPS

Do you have any data on the evaporation rate of moisture in the drum granulator and to what degree does the use of countercurrent sweep of air enhance evaporation?

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

We have studied slurry process TSP operation and come to the conclusion that for the case of a plant producing 40 to 50 MT/ha about 2 T/hr evaporation of water takes place in the granulator. For DAP operation evaporation amounts to about 1.2 tons per ton of liquid ammonia absorbed in the granulator. Indications are that countercurrent sweep of air enhances evaporation. For urea grades by evaporating water as the heat is required to compensate for the drop in temperature due to urea going into solution.

Q - Mr. K.D. SHAH (Imperial Chemical Industries Ltd, U.K.)

In the paper (bottom of p. 21-3) a comparison is made between the drying times and the % moisture removed for several different process plants to indicate the importance of the slurry feeds. (see fig. 1). This appears to be a rather simplified approach to a complex drying phenomenon. Drying time depends on factors such as gas rate, solids temperature and the terminal moisture levels. The actual levels of moisture are more important than the % moisture removed. I would like to ask if the above factors were comparable in the examples quoted.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

We admit the drying retention curves presented are an oversimplification of the situation. However, they are for several plants which were designed by Dorrco and represent similar quantities of air per ton of water evaporated and therefore similar drying driving forces.

Also the products were stable and in good conditions for the moisture reported. Our point is that these detentions appear to be shorter than data previously published.

Q - Mr. K.D. SHAH

Two important points made about the slurry process are that the granulation in this process is primarily by layering technique and that the granules thus produced are easier to dry than the material produced by agglomeration. I have two questions in this area: the first one: Has any quantitative study been done to assess the relative proportions of the two, e.g. by microscopic examination of the cross-section of the granules. In our experience at ICI, the extent of agglomerative granulation on a blunger with some slurry feeds is not insignificant and varies from formulation to formulation.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

Yes, we agree that many formulas do require substantial agglomeration to accomplish granulation and again we are oversimplifying. We have done no microscopic examination.

Q - Mr. K.D. SHAH

Second question: Taking the above point a little further one would expect a drum granulator to give a relatively higher degree of layering granulation than a conventional blunger due to the gentle rolling action and higher residence time in a drum. If what is suggested in the paper is valid, one would expect, therefore, a drum granulated material to require a shorter drier than the blunger granulated material of the same composition from the same feeds.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

We design for same dryer retention whether a granulator or blungers are used.

Q - Mr. K.D. SHAH

Some Dorrco plants have two units side by side working on common feeds, one with blunger and one with drum granulators. I would welcome the authors' comments on the observations made on such units in terms of the above.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

A comparison of the blunger line with the granulator line side by side indicates a preference for the granulator at least for DAP. Both capacity and product mol ratios are higher for the TVA type granulator.

Q - Mr. I.K. WATSON (UKF, U.K.)

Relating to choice of use of blunger versus drum granulator and to your answer related to DAP where ammoniation is required in the granulator. However in the case of NPK's where a slurry with mole ratio of 1.4 and further ammoniation is not required, what is the advantage

of drum granulator over a blunger? I get the impression that you now favour drum granulators rather than blungers which was not formally the case.

A - Mr. D.W. LEYSHON and Mr. I.S. MANGAT

Yes, the paper does seem to give this impression probably because most of comparative data given relates to drum granulators. We have however recently made a plant proposal based on a blunger and we do not really have any preference for drum granulator. Generally the choice reflects customer preference. Madras Fertilizer Ltd. in India have now added a third line to the originally two train Dorrco plants. This train uses a blunger and the choice was made after operating experience in the original trains one of which features a blunger and the other a drum granulator.

4th Working Session: Pollution abatement in the fertiliser industry

TA/76/1 Process for recycling H_2SiF_6 solutions recovered by gas washing, to the den of superphosphate by R. MONALDI, G. VENTURINO, Montedison SpA, Italy (Rapporteur M. BONGARD, Windmill Holland, Netherlands)

Q - Mr. A.B. PHILLIPS (TVA, USA)

1. How does the cost of operation compare with and without recycle of H_2SiF_6 ?
2. Does recycling H_2SiF_6 increase F evolution in the curing building or increase corrosion of equipment such as mixer and den?

A - 1. With recycle of H_2SiF_6 the cost of operation is reduced by about US \$ 0.5 per ton of superphosphate, mainly because of the reduced H_2SO_4 consumption. To this reduction it has to be added the one coming from the saving of a man per shift. It has also to be considered that it is no more necessary to transform the H_2SiF_6 , with related pollution problems. This last fact gave in 1973 a benefit of about US \$ 0.5 million for all the Montedison superphosphate plants. As far as investment costs are concerned, we can consider two cases:

- for existing plants the H_2SiF_6 recycle requests small modifications, limited to the installation of a pump and a metering device for the acid recycling, with obviously moderate costs;
- for new plants, against the said moderate charges there is the considerable saving due to the elimination of filters and neutralization and disposal equipments for the silica, that are no more necessary.

2. As far as the F evolution in the curing building is concerned the answer is negative because, with or without recycle of H_2SiF_6 , the watersoluble F content in superphosphate (responsible for the F vapours evolution into the atmosphere) is the same. In fact in the case of H_2SiF_6 recycle the additional F is present in superphosphate in the CaF_2 stable form.
As far as corrosion is concerned, please see the following answer.

Q - Mr. G.A. MENIN (Perfosfatì Cerea, Italy)

Do you have corrosion in the mixer in which H_2SiF_6 solutions are recycled? Which material do you use?

A - Actually the corrosion problem has been the most difficult to be solved and concerned essentially the mixer. Tests have been made on various materials till the solution of the problems was reached. At the present time the fixed parts of the mixer are made of Ni-Resist austenitic cast iron.
On the other hand, the moving parts are made of austenitic high-alloy, very low-carbon steel.
No corrosion problems have been noticed in the den.

Q - Mr. K.L. PARKS (Agrico, USA)

Do you think this process could be extended to the triple superphosphate process?

A - This process can be extended also to triple superphosphate production, with minor problems than in the case of single superphosphate; in fact Montedison has already applied it in one of its triple superphosphate plants.

Q - Mr. J.L. BOTHA (Fedmis, South Africa)

1. What construction material is used for the scrubber system?
2. What method is used to determine the F-concentration in the stack gases?

A - 1. The material used for the construction of the scrubber system is Moplen (polypropylene Montedison).
 2. Fluorine is collected with the usual laboratory equipments (Drechsel bottles, etc.) in 0.1 N NaOH solution. The determination is then made according a method developed by the Fertilizer Research Center of Montedison (Method C.R.F. n. 80040), described in the Enclosure A.

Q - Mr. N. COUVAS (S.A. Hellénique de Produits et Engrais Chimiques, Greece)

1. As it is said in your communication with the recycling system of H_2SiF_6 , the superphosphate produced has a 0.2% lower percentage. Have you done successful trials to ameliorate this disadvantage or the proposed stronger sulfuric acid etc are theoretically only examined?
2. As emission of fluorine when recycling is 3 times more, the question is if it is possible to treat at the same time gases coming from superphosphate plant and a classical phosphoric acid unit producing 28-30% phosphoric acid, in order to solve both pollution problems. Have you done any experiments on this case?

A - 1. The use of stronger H_2SO_4 to obviate the lowering of 0.2% in the superphosphate grade has been practically tested when rocks of lower grade have been acidulated. In this way it has been possible to suppress the 0.2% loss in the grade of the produced superphosphate.
 2. Test of recycling additional H_2SiF_6 coming from a H_3PO_4 unit have not been made, but theoretically speaking, considered the good physical characteristics of the superphosphate obtained with recycle of H_2SiF_6 , we think it possible to increase the amount of H_2SiF_6 recycled, experimentally finding out the optimal operating conditions.

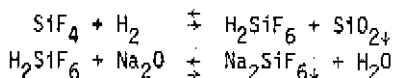
Q - Mr. M. BONGARD

How much additional H_2SiF_6 e.g. from a phosacid evaporation plant can be disposed of in the super plant?

A - The additional amount of H_2SiF_6 that can be recycled depends upon many factors. The limiting conditions can be defined only experimentally.

Q - Mr. A.M. VERDASCA (C.U.F., Portugal)

1. It is well known that the absorption reaction of SiF_4 through fluorine recovery follows the reactions:



Silica and sodium fluosilicate produced tend to scale and to clog scrubbers and their spray nozzles, as well as the inlet and outlet air ducts, etc.

How did Montedison solve that problem? Why did Montedison not use the Venturi scrubber? In any case we would be pleased to know the capacity of your plant in t/d H_2SiF_6 and the recovery efficiency of each tower as well as the flow- and feed-rate of gas feeding to the recovering plant?

2. Since H_2SiF_6 recycling can increase the amount of fluorine to be recovered in the plant and that the efficiency of recovery in the Montedison towers is high, what is the number of mass transfer units checked in the towers, the pressure on the nozzles as well as the height of the former?

A - 1. Montedison makes the fluorine absorption only with water so that the problems mentioned, caused by sodium fluosilicate, do not exist. As precipitated product there is only SiO_2 , but we can assure that with the absorbing system adopted, the troubles mentioned by Mr. Verdasca are not met. The use of the Venturi scrubber, adopted in the past in some plants, on the contrary caused the said troubles. Other data requested are as follows:

- Capacity of the absorbing section: about 18,000 kg/d of H_2SiF_6 100%;
- Absorbing efficiency: about 80% at the outlet of the first tower; about 96% at the outlet of the second tower; more than 99.5% at the outlet of the third tower;
- Gas fed to the absorbing section is between 8,000 and 12,000 Nm^3/h ;
- Gas speed at the inlet of the absorbing section: about 8-12 m/sec.

2. The number of transfer units is given by the equation (see the study of A.G. Calver and J.D.C. Hemsley "The Design of Void Spray Towers for Silicon Tetrafluoride Absorption", Proceedings n. 63, Fertiliser Society, London 27th October 1960)

$$N = \ln \frac{y_1 - y^*}{y_2 - y^*}$$

On the basis of this equation, of the equilibrium diagram of Fig. 4 and of data reported in Tab. 3, the value of N can easily be found. Spray nozzles are of particular type, with low pressure top.

Q - Mr. P. MORAILLON (G&S, France)

- The space between the grids, as stated in p. 6, is 1 cm only. Is it correct?
- Can we get additional information on the concept of the grids, the gas flow-rates, the demisting systems?
- Does the watering flow-rate indicated, 5000-6000 l/m²/hr. relate to each spraying stage every 3 m or to the total liquid flow-rate?
- What are the inlet and outlet fluorine contents in the towers? Are droplets carried over?

A - In the Paper it is said, because of a translation mistake, that the distance between the grids is of 1 cm. In reality 1 cm is the spacing of the grids elements.
Tower sizes and gas feed rates are a function of the process variables. The liquid wetting rate of 5000-6000 l/m² refers to each spraying stage.
Fluorine inlet and outlet contents from the towers can be found in Tab. 3.
A column that does not cause carry over of droplets has been realized, and so demisters are not needed.

Analytical Method C.R.F. n. 80040

Fluorine determination in basic solutions of gas absorption.

The fluorine content in stack gases from a superphosphate plant is determined by absorbing a known volume of gas in 0.1 N NaOH solution and determining the fluorine collected in said solution.

Apparatus

- a) Digital pHmeter - Orion Model 701 or equivalent
- b) Fluorine electrode - Orion Model 94 - 09
- c) Single junction reference electrode - Orion Model 90 - 01
- d) Magnetic stirrer

Reagents

- a) Potassium fluoride - Primary grade
- b) N sulfuric acid
- c) Buffer solution - Dissolve 294 gr of tribasic sodium citrate dihydrate in 1 liter flask by distilled water and add 5 M HCl reaching pH 6.0.
- d) Distilled water.

Calibration

Prepare a set of standards containing from 0.1 to 20 ppm fluoride ion in 4 ppm increments. Place 50 ml of each standard in 150 ml beaker. Add 50 ml buffer solution. Add stirring bar, place on magnetic stirrer and immerse electrodes in solution of first standard. Record potential. Repeat measurements for other standards. Report data on semi logarithmic diagram obtaining a calibration curve.

Procedure

To basic absorption solution add some few drops of methyl orange as indicator.

Neutralize by H_2SO_4 1N, and dilute to 1000 ml.

Measure potential of standard solution 20 ppm (diluted 1+1 by buffer solution).

By potential calibration bottom regulate response of standard solution to the same value put in calibration curve.

Transfer 50 ml of sample solution in 150 ml beaker adding 50 ml buffer solution and measure potential.

By calibration curve find sample concentration whose value corresponds to fluoride mgs gathered during sampling.

Results

$$\text{mg/m}^3 = \frac{\text{mg}_c}{\text{m}^3_c}$$

where

mg_c = milligrams per liter of fluoride in sample solution.

m^3_c = cubic meter of sampled gas.

TA/76/2 Safety in rotary dryer operation by G. PERBAL, UKF, Netherlands
(Rapporteur M. BONGARD, Windmill Holland, Netherlands)

Q - Mr. H. GÖLLER (Chemie Linz, Austria)

Mr PERBAL, you are writing in your paper that a high inlet temperature in the rotary dryer, respectively spherodizer, may start off, in case of malfunctioning of the equipment, a spontaneous heating of the entire mass in the dryer and you are concluding from this that for safe operation:

- product temperature should be maintained not higher than 105°C, and
- the inlet flue gas temperature not higher than 160°C.

It is of essential importance for the avoidance of spontaneous decomposition in the dryer to limit product temperature, which is correctly adjusted at approximately 105°C. However, to maintain product temperature not the inlet flue gas temperature but the outlet temperature is essential. At Chemie Linz, with a view to avoid spontaneous decomposition the outlet temperature of the heating gas is measured and recorded by 2 meters (resistance thermometers) operating independently from each other. When the outlet temperature exceeds the adjusted nominal value, first a warning signal is given by the first meter and subsequently the switching off of firing is released by the second meter. The cold air stream remains in operation.

Provided the dryer gets the necessary quantity of heat for maintaining the required outlet temperature, the level of inlet temperature is compulsorily resulting.

A limitation of the said inlet temperature is given by technological reasons and is determined by the properties of the product (pH-value, melting point, water contents of slurry, composition of formulation, water solubility, etc.). As a matter of fact, the inlet temperature, which is generally by far higher than 160°C, may cause decomposition of crusts, respectively deposits in the dryer. But this decomposition is proceeding slowly in accordance with the values found in the trough tests and is easily controlled.

A - I should like to start with your last question concerning the 160°C. In my introduction to my paper I already pointed out that the inlet flue gas temperature may be higher if adapted to the hazard profile of the product.

Listening to your explanation of your safety system, guarding your equipment, I should say that this will be all right. Nevertheless it might be helpful to have also a temperature indicator with alarm on the inlet flue gases.

Q - Dr. W. BOOS (Gewerkschaft Victor, Germany)

One of your safety measurements is the limitation of the inlet flue gas temperature. Since the start of a decomposition is dependent on the product temperature itself I think that your suggestion is not the best solution. In my opinion it should be better to measure the outlet product temperature and the outlet flue gas temperatures and control with these two the operation of the dryer.

A - Due to the long response time when measuring the product temperature, I fear that this will give an unacceptable delay in the alarm. Concerning the 160°C I should like to refer to my answer to Mr. Göller.

Q - Dr. G. SIEBERT (BASF, Germany)

In connection to what Dr. Boos already said I should like to explain that BASF has taken a number of other valuable safety measurements, with good results.

Automatic shutdown of the burners occurs:

- when the dryer stops
- when the exhausters stop
- when there is not enough low pressure
- manual operated push-button for emergency stops

Next to these measurements, an automatic reduction in temperature of the flue gases occurs in case of:

- interruption of the product feed
- interruption of the recycle and
- during the start up period.

Since the time that this equipment is in use, more than 4 years ago, BASF has experienced no decomposition in the equipment.

A - It has to be remarked that there are of course more safety systems possible which give satisfactory safeguarding. The intention of this paper is that those who are present here will reconsider the safeguarding of their equipment at home.

This paper shows you the way how you can tackle the problems.

Q - Mr. W.H. COATES (Albright & Wilson Ltd, United Kingdom)

Does this apply to all nitrophosphate processes?

A - It applies to all fertilizers containing ammonium nitrate and chloride ions.

Q - Mr. P. ROLFSEN (Norsk Hydro, Norway)

If you operate the drum co-currently can you obtain satisfactory capacity when the flue gas temperature is restricted to 160°C?

You recommend the NPK type 16+11+14 to be deleted as unsafe. We do not agree here, as our 16+11+14 already is a safe one, i.e. not liable to self-sustaining decomposition.

A - When answering your first question I should say that it is a matter of the design of the dryer. As already mentioned in my paper it can give difficulties for existing equipment.

In my paper I mean products as hazardous as the investigated 16+11+14. It is not my intention to ban certain formulations but to ban products which are very hazardous. As you know the degree of hazard you can't read from the formulation. As a consequence your 16+11+14 is not made of the same raw materials.

Q - Mr. K.C. KNUDSEN (Superfos, Denmark)

In your summary - page 28 - you recommend

- inlet flue gas temperature not higher than 160°C as a general rule. However, on page 29 you say: "When operating at temperatures of 180°C and higher, hazardous products like 16+11+14 have to be deleted from the production program",

So why not write specifically:

- inlet flue gas temperatures not higher than 160°C when type B fertilizers are being produced?

A - I think that your suggestion is too stringent. Also among type B products there is a wide variety of sensitivity to self-sustaining decomposition. For this reason I should like to emphasize that the dryer operating conditions have to be adapted to the hazard profile of the product involved. The hazard profile can be evaluated by the aid of the ISMA/APEA-test methods as mentioned on page 28 of my paper.

TA/76/3 The use of phosphogypsum by B. NEVEU, CdF Chimie, France (Rapporteur D.C. OOSTERWIJK, UKF, Netherlands)

Due to lack of time, some of the questions could not be answered during the discussion after Mr. Neveu's paper, but are still included below.

Q - Type of Phosphate - Mr. A. KABIL (Donau Chemie, Austria)

A - It is not possible to confirm that the process is suitable for all

phosphates as for each individual case direct experience is required, at least on laboratory scale and, even better, on pilot plant scale. CdF Chimie have industrial experience in their Douvin plant with gypsum, originating from Florida rock Agrico 72, 70 and even 68 BPL and Khouribga rock 75 BPL. They have pilot plant experience with gypsum from Taiba, Gafsa, Kola and Bucraa rocks.

- Q - Purification - Messrs
- | | |
|---------------|------------------------------|
| A. KABIL | (Donau Chemie, Austria) |
| K.L. PARKS | (Agrico, USA) |
| H. KURANDT | (Veba Chemie, Germany) |
| N. ROBINSON | (Fisons Ltd, U.K.) |
| P.F. KAVANAGH | (NET, Ireland) |
| O. JENSEN | (Superfos, Denmark) |
| N. COUVAS | (Société Hellenique, Greece) |
| R. KREMPFF | (Cerphos, France) |
| M.G. GAURON | (Cofaz, France) |

- A - The overall efficiency of the purification section depends on the number of hydrocyclone stages and varies with the morphology and crystal size of the gypsum. It lies between 75 and 90%.

The percentages of the principal impurities in the gypsum, before and after purification, based on the dry product, are given below.

The figures apply mainly to gypsum, obtained in single-stage crystallization phosphoric acid plants.

		Raw Gypsum	Purified Gypsum
P ₂ O ₅	total	0.90 - 1.2	0.55 - 0.65
	soluble	0.15 - 0.4	< 0.02
	co-crystallized	0.4 - 0.6	0.4 - 0.5
	unreacted	0.1 - 0.45	0.05 - 0.15
F	total	0.8 - 1.0	0.6 - 0.7
	water-soluble	0.1 - 0.2	< 0.01
Na ₂ O		0.25 - 0.5	< 0.04
C	(organic matter)	0.1 - 0.4	< 0.02

No precise measurements of the gypsum attrition in each stage of the purification section have been carried out. The total attrition in the whole purification section is, however, negligible.

The waste water from the purification section contains the acids and soluble salts extracted from the gypsum and also organic matter and very fine gypsum crystals. At Douvrin, the water is neutralised with chalk, flocculated, clarified and discharged (within the French anti-pollution standards).

If there is a water-problem, two solutions are possible:

- recycling of part of the acid water, after removal of the solid materials, to the phosphoric acid plant;
- recycling of part of the neutralized and clarified water to the gypsum purification section.

- Q - Gypsum filtration - Mr. K.D. SHAH (I.C.I., U.K.), Mr. K.L. PARKS

A - To separate the large grains from the gypsum slurry, sieve plates are used, developed by the French Bureau de Recherche Géologique et Minière. The percentage of unreacted phosphate, removed on the sieve plate, depends on the characteristics of the phosphate used and the operating conditions in the phosphoric acid plant. At Douvrin, when using Florida rock 70 - 72 BPL, the percentage of P_2O_5 (as unreacted phosphate) removed by the sieve plates is about 0.2% - 0.3%, based upon the weight of the dry raw gypsum. The economics of recycling this phosphate to the phosphoric acid plant has not been studied. Most probably, grinding would be necessary.

The filtrability of the purified slurry is much better than that of the gypsum slurry in the phosphoric acid plant, due to the lower viscosity of the liquid phase, the absence of organic matter and the removal of the smallest particles in the hydrocyclones. About 0.50 m² filter area per ton/hour of gypsum is used.

Q - Drying of gypsum - Mr. R. KREMPFF, Mr. T. McCARTY (NET, Ireland)

A - At the outlet of the dehydrator, a mixture of β -hemihydrate and anhydrite III is obtained, not because the treatment is not homogeneous, but because of the temperature and humidity of the drying gas. The thermal treatment of gypsum in a stream of hot unsaturated air always results in such a mixture. Depending on the operating conditions of the dehydrator, the %age of anhydrite III at the outlet of the dehydrator can vary from 30 to 70%. In the third drier, the product is contacted with humid lukewarm air, resulting in a complete conversion of the anhydrite III to hemihydrate and the recovery of the heat of transformation. The percentages of gypsum and anhydrite II in the final product are less than the limits of detection of X-ray diffraction methods.

Q - Application - Messrs R. KREMPFF, H.F. KURANDT, N. COUVAS

A - Due to the homogeneous thermal treatment, the plaster has very uniform characteristics. Without any additives (water/plaster ratio 0.8) setting starts in 1½ - 2 minutes and has fully set in 6 - 8 minutes. By adding retarding agents, these characteristics can be varied within very wide limits. For a specific application of Douvrin plaster, the setting time was increased to 60 min. without harmful effects on the mechanical resistance.

The plaster manufactured at Douvrin has a fine granule size, especially due to a final grinding operation to control its rheological properties. The daily production is between 300 and 350 tons of plaster which is practically all used for the manufacture of boards. The boards compare favorably, from a quality point of view, with identical products from plaster ex natural gypsum, a fact which is acknowledged by the official organisations of the French building industry.

With regard to utilisation of phosphogypsum as an additive to Portland cement, Cdf's experience is:

a) Unpurified raw gypsum from single-stage crystallization phosphoric acid plants is not suitable as a cement additive, even after neutralization with lime;

- b) The same gypsum, after purification, can usually be used for the above purpose but a definite answer can only be given if the composition of the cement in question is known;
- c) Gypsum obtained in double crystallization phosphoric acid plants and purified in the CdF process; always gives results which are very close to those obtained with natural gypsum.

A/76/5 Windmill Holland and its environment by N.W. KOLMEIJER and J.H. WISSINK, Windmill Holland, Netherlands (Rapporteur D.C. OOSTERWIJK, UKF, Netherlands)

- Q - Scrubbers - Messrs P.L. BALDWIN (Cremer and Warner, U.K.)
 - I. MINI (Montedison, Italy)
 - R. MONALDI (Montedison, Italy)
 - J. MASSART (U.C.B., Belgium)

A - Although, for new plants, Windmill would not design scrubbers themselves, in cases where existing scrubbers could be modified, it was more attractive to do the job themselves. They simply "put grids and balls in" and found that the system worked satisfactorily. The scrubber-condenser for the phosphoric acid filter system was also designed by Windmill. The scrubbers of the self-induced spray-type are proprietary items of equipment, in which the air closely skims a liquid surface causing the liquid to be finely distributed into the air so that no spray or circulating systems are required.

The scrubber effluents are discharged into the river. Regarding recirculating them to the granulator, even if they were concentrated as much as possible, would affect the capacity of the extremely low recycle granulation plants, too much.

Up to the present, the favoured system for dust control in the off-gases from driers and coolers was cyclone batteries, followed by wet scrubbers. However, since 1971 ever increasing penalties have to be paid for the discharge of oxygen-consuming materials and this may change the situation in favour of bagfilters.

- Q - Levels of emissions - Messrs J. MASSART, S. ORMBERG (Norsk Hydro, Norway), I. MINI

A - In the Netherlands, the Nuisance Act and the Act on Air-Pollution apply, in which no firm figures are given. The authorities base their demands on:

- a) best practical means;
- b) legislation abroad;
- c) other relevant factors, such as further existing emissions on the site and in the neighbourhood.

The resulting demands by the authorities are nowadays usually very strict.

On water-pollution a similar situation exists.

The detector used for N_2O is a URA-202 non-dispersive infrared absorption meter, manufactured by MSA. The detector is of the membrane-type.

Q - Cost of environmental protection - Mr. E. UUSITALO (Kemira Oy, Finland)

A - In general it is very difficult to separate the investment required for environmental matters from the total investments for projects. However, in the last few years, Windmill have an annual budget of DF1 500,000, = for small items, such as improved grabs, wind measuring equipment, samplers, N_2O -detection meters, noise-measuring devices, Rodiscopes, etc. The money is used for purchasing the equipment, hours spent by Windmill mechanics, etc. The salary of the environmental officer is e.g. not included.

Q - Hazardous materials - Messrs R. MONALDI, A.M. McLEOD, I. MINI

A - Stabilizing salts (e.g. magnesium salts) to reduce the risk of self-sustaining combustion are not used by Windmill. If a new grade of compound is of the B-type, we try to change the raw materials in order to produce a C-type, using the triangular diagrams as described in the Fertiliser Society Proceedings, N° 124.

When a producer or user of B-grade fertilizer asks for a permit under the Nuisance Act, rules laid down by industry and government for the storage of AN-containing fertilizers are applied.

Manufacturers can store a B-type in bulk in units up to 3,000 tons. For traders and users these quantities are 1,000 tons. With adequate separation (at least 2,5 m space) and provided the shed has been built according to certain regulations regarding electrical installation and fire protection, more units can be stored in one shed.

Gewerkschaft Victor has developed a water lance, recommended for "in silo" extinguishing. The value of the lance has been fairly well proven in incidents. The lance consists of a tube with a head with specially designed holes. Water consumption is 280 l/min at a pressure of 80 m head. At this quantity and pressure, the lance penetrates easily in the fertiliser and stops the decomposition when the water reaches the right spot. Details are given in the ISMA/APEA handbook "Storage of Ammonium Nitrate". (Reply by Dr. W. Boos of Gewerkschaft Victor).