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THE CROS NPK PROCESS

Use of the cheapest raw materials, and better
raw materials recovery

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1. INTRODUCTION

The present situation on the international raw materials market and the latest price increases require that the manufacture of fertilizers be optimized so as to minimize the contribution of the raw materials to the total manufacturing cost.

We can attain this goal in two ways :

- a) by choosing cheaper raw materials
- b) by maximizing efficiency

The present report shows the results obtained in the manufacture of NPK fertilizers according to the CROS process. Use is made of cheap raw materials - 18 % and 45 % (TSP) superphosphates, ammonia, urea, by-product acids, etc. - with yields over 99 %. The process operates in such a way that all the wash liquors are recycled and environmental pollution problems are virtually nonexistent.

In most countries legal regulations require that deviations of the actual concentration from the posted composition be kept to such a minimum that a fertilizer manufacturer prefers to waste expensive raw materials in order to be on the safe side, statistically speaking, on account of the large deviations which may arise in any granulation process.

The CROS process avoids this pitfall by making use of a servoanalyser for the analytical control of production through a statistical correction technique.

2.- PROCESS DESCRIPTION

Figure 1 shows a typical process flowsheet. Points worth noticing are the arrangement for intensive ammoniation inside the granulating bed and the gas scrubbing equipment.

2.1. Equipment for intensive ammoniation

The equipment has been described in an earlier report submitted to the ISMA Conference held in Seville in 1972 (1).

The major advantages are :

- a) High degree of direct ammoniation in the granulating bed. More than 100 Kg ammonia/tonne NPK can be fed to the granulating bed. More than 90 % of this ammonia is actually retained by the bed and the rest is scrubbed out with acid wash and recycled to the granulator.
- b) Direct neutralization of sulphuric and phosphoric acids in the granulating bed. No preneutralizers are required nor any intermediate slurry has to be handled.
- c) Granulation of formulations with high urea and superphosphate contents with no need of high recycle rates.
- d) High granulation efficiencies call for very simple installations with equipment actually smaller than in conventional plants of the same rated capacity.

The CROS process has achieved its results through special care in the design of some key points.

These are :

2.1.1. Pregranulator

Basically a conventional pan or drum granulator but equipped with our special ammonia injection equipment. This pregranulator has been specifically designed for the following tasks :

- a) To effect pregranulation. This is a low-temperature, low-humidity operation in which the granules tend to agglomerate while empty hollows remain.
- b) To humidify the solids in order to prevent dust formation at the granulator inlet.

- c) To partially ammoniate the superphosphate present in the fertilizer. This is important whenever superphosphate and urea mixtures are granulated because ammoniation prevents the formation of a urea-monocalcium phosphate adduct with release of hydration water which would cause excessive over-granulation.(2)

2.1.2. Reactor/Granulator

It consists of a rotary drum furnished with our special ammonia injection equipment. A thorough ammoniation and neutralization of sulphuric and/or phosphoric acid take place in this reactor. The granulation is carried out through a "layering" process. Each granule acts like a small individual reactor, the ammonia reacting with the liquid phase on its surface.

The temperature increase which results from the exothermic reaction causes the solubility of the salts to increase and a more concentrated liquid phase appears which has a lower surface tension.

This liquid phase fills up the hollows left in the grains from the pregranulator and the granule diameter increases as a result of the formation of successive layers which dry up and crystallize at these high temperatures.

We obtain more compact, rounder granules with better handling and storage properties.

The distribution of the ammonia and acid inlet nozzles is an important design feature of the granulator. Generally speaking we fit an entrance section in which the raw materials are moistened with acid; the ammonia injection nozzles are arranged along an intermediate section which extends for about 2/3 of the reactor. This intermediate section is also fitted with additional acid spray nozzles. The end section is empty and acts as a finishing and drying section.

2.1.3. Tubular reactors

Whenever it might be in our interest to increase the ammonia feed rate (say, for example, in formulation with over 100 kg NH_3 /tonne, as is the case in the MAP, DAP, and urea-sulphate manufacture) it is advisable to use a tubular reactor for the direct neutralization of sulphuric and phosphoric acid with ammonia. The product from this reactor is a partly neutralized slurry of ammonium salts. This slurry is poured on the pregranulator where the ammoniation is completed.

This tubular reactor has been described in detail elsewhere (1). Its standard capacity is about 300 Kg/h of liquid ammonia.

The granulation temperature is controlled by evaporating excess water by regulating the flow of air through the granulator. Thus an optimum temperature can be reached to maximize the ammoniation of all phosphates present in the mass while urea decomposition is prevented.

Since the temperature is at least in part regulated by means of water evaporation, all the scrubber effluents can be recycled to the granulator and no pollution problems arise. Additional high recycle rates are not needed (the recycle ratio is between 1 : 1 and 1 : 2) so that the remaining equipment can have a smaller size. This size reduction is especially important as far as the drying equipment is concerned : the product comes out of the granulator at fairly high temperatures (70-80° C) and with a low water content (2/3%) which implies sizeable savings in fuel consumption.

2.2. Gas scrubbing equipment

All gases from the granulator and the dryer are washed in Venturi-type scrubbers. The flow of water required is very small, slurries with up to 100 g/l can be handled, and the dust collection efficiency is high. The exit gases carry less than 15 mg/m³ particles in suspension.

Dust emissions can thus be reduced to levels lower than those allowed by law while all the wash liquors are recycled back to the granulator. Recovery of raw materials in the dust is up to 98-99 %.

3. RESULTS

Tables 1 to 4 show the results obtained in actual production runs for several typical NPK fertilizer formulations. The plant on which these results were obtained has a designed capacity of 20 tonnes/h. Data on the manufacture of DAP and a 28-28-0 (phosphoric acid and urea) are included.

TABLE N° 1

Composition : 15-15-15
 Production : 20 tonnes/h

Granulator

<u>Inlet :</u>	Liquid ammonia	1,730 Kg/h
	prilled urea	3,520 "
	45% superphosphate	6,700 "
	potassium chloride	5,100 "
	recycle	32,000 "
	scrubber liquor	6,552 "
<u>Outlet :</u>	outlet temperature	80° C
	outlet humidity	3.8 %

DryerSolid phase :

	inlet temperature	80° C
	outlet temperature	70° C
	inlet humidity	3.8 %
	outlet humidity	1.6 %
	Screen size	
	over 4 mm	13.7 %
	2-4 mm	25.0 %
	1-2 mm	30.3 %
	under 1 mm	31.0 %

<u>Air :</u>	inlet temperature	200° C
	outlet temperature	75° C
	flow rate	37,800 m ³ /h
	fuel consumption	150 Kg/h

Granulator scrubber

<u>Inlet :</u>	NH ₃ from granulator	105 Kg/h
	sulphuric acid 78%	5,630 "
	liquor from dryer scrubber	1,424 "
<u>Outlet :</u>	liquor to granulator	6,552 kg/h
	temperature	49° C
	composition N	1.87 %
	H ₂ SO ₄	62.3 %
	NH ₃ losses	10 Kg/h

Driver scrubber

<u>Outlet</u> :	liquor to granulator scrubber	1,424 Kg/h
	composition	
	N	3.16 %
	P_2O_5	1.41 %
	K_2O	2.18 %

ProductComposition :

N	15.07 %
P_2O_5	14.95 %
K_2O	14.96 %
H_2O	1.6 %

Screen size :

over 4 mm	0.5 %
2-4 mm	65.0 %
1-2 mm	34.0 %
under 1 mm	0.5 %

Overall efficiency :

N	99.2 %
P_2O_5	99.1 %
K_2O	99.5 %

TABLE N° 2

Composition :	6-12-24
Production :	25 tonnes/h

Granulator

<u>Inlet</u> :	liquid ammonia	1,475 Kg/h
	MAP	2,800 "
	18 % superphosphate	8,635 "
	potassium chloride	10,040 "
	recycle	24,000 "
	scrubber liquor	4,772 "

Outlet : outlet temperature 82° C
outlet humidity 6.1 %

DryerSolid phase :

inlet temperature 82° C
outlet temperature 80° C
inlet humidity 6.1 %
outlet humidity 2.4 %
screen size
 over 4 mm 9.5 %
 2-4 mm 37.5 %
 1-2 mm 40.5 %
 under 1 mm 12.5 %

Air : inlet temperature 350° C
outlet temperature 90° C
flow rate 39,500 m³/h
fuel consumption 180 Kg/h

Granulator scrubber

Inlet : NH₃ from granulator 81 Kg/h
sulphuric acid 78 % 3,307 "
liquor from dryer scrubber 2,150 "

Outlet : liquor to granulator 4,772 Kg/h
temperature 52° C
composition N 1.60 %
 H₂SO₄ 48.0 %
NH₃ losses 5 Kg/h

Dryer scrubber

Outlet : liquor to granulator scrubber 2,150 Kg/h
composition N 0.44 %
 P₂O₅ 0.68 %
 K₂O 1.80 %

ProductComposition :

N	6.02 %
P ₂ O ₅	11.98 %
K ₂ O	24.01 %
H ₂ O	2.4 %

screen size :

over 4 mm	0.1 %
2-4 mm	73.8 %
1-2 mm	25.8 %
under 1 mm	0.3 %

Overall efficiency :

N	99.1 %
P ₂ O ₅	99.4 %
K ₂ O	99.6 %

TABLE N° 3

Composition : 18-46-0 (DAP)

Production : 12 tonnes/h

Tubular reactor (Each)

<u>Inlet :</u>	liquid ammonia	300 Kg/h
	45% phosphoric acid	3,466 "
<u>Outlet :</u>	reactor slurry	3,616 Kg/h
<u>composition :</u>	N	6.80 %
	P ₂ O ₅	43.12 %
	H ₂ O	26.42 %

Pregranulator

<u>Inlet</u> :	liquid ammonia	300 Kg/h
<u>-----</u>	reactor slurry	7,232 "
	recycle	45,000 "
<u>Outlet</u> :	composition N	16.74 %
<u>-----</u>		
	P ₂ O ₅	47.39 %
	H ₂ O	4.99 %
	outlet temperature	80 ° C
	NH ₃ losses	20 Kg/h

Granulator

<u>Inlet</u> :	liquid ammonia	1,744 Kg/h
<u>-----</u>	pregranulator product	52,312 "
	liquor from granulator	
	scrubber	5,575 "
<u>Outlet</u> :	outlet temperature	80 ° C
<u>-----</u>	outlet humidity	4.62 %
	NH ₃ to scrubber	160 Kg/h

DryerSolid phase :

	inlet temperature	80 ° C
	outlet temperature	75 ° C
	inlet humidity	4.62 %
	outlet humidity	2.01 %
<u>Air</u> :	inlet temperature	300 ° C
<u>---</u>	outlet temperature	80 ° C
	flow rate	38,700 m ³ /h
	fuel consumption	160 kg/h

Granulator scrubber

<u>Inlet</u> :	NH ₃ from granulator	160 Kg/h
	phosphoric acid 50 %	4,881 "
	liquor from dryer scrubber	890 "
<u>Outlet</u> :	scrubber liquor	5,575 Kg/h
	composition N	2.20 %
	P ₂ O ₅	43.78 %
	NH ₃ losses	10 Kg/h

Dryer scrubber

<u>Outlet</u> :	liquor to granulator	890 Kg/h
	composition N	2.80 %
	P ₂ O ₅	2.39 %

ProductComposition :

N	17.86 %
P ₂ O ₅	46.16 %
H ₂ O	2.01 %

Screen size :

over 4 mm	0.0 %
2-4 mm	58.6 %
1-2 mm	41.1 %
under 1 mm	0.3 %

Overall efficiency :

N	98.9 %
P ₂ O ₅	99.6 %

TABLE N° 4

Composition : 28-28-0
 Production : 25 tonnes/h

Granulator

<u>Inlet</u> :	liquid ammonia	1,972 Kg/h
	urea	11,885 "
	recycle	35,000 "
	scrubber liquor	14,825 "
<u>Outlet</u> :	outlet temperature	70° C
	outlet humidity	3.5 %

DryerSolid phase :

	inlet temperature	70° C
	outlet temperature	70° C
	inlet humidity	3.5 %
	outlet humidity	1.5 %

<u>Air</u> :	inlet temperature	200° C
	outlet temperature	75° C
	flow rate	37,800 m ³ /h
	fuel consumption	150 Kg/h

Granulator scrubber

<u>Inlet</u> :	NH ₃ from granulator	160 Kg/h
	phosphoric acid 50 %	14,136 "
	liquor from dryer scrubber	1,106 "
<u>Outlet</u> :	liquor to granulator	14,826 Kg/h
	composition N	0.95 %
	P ₂ O ₅	47.88 %
	H ₂ O	25.8 %
	NH ₃ losses	15 Kg/h

Dryer scrubber

<u>Outlet :</u>	liquor to granulator scrubber	1,106 Kg/h
	composition N	2.09 %
	$P_{25}O_5$	2.80 %

ProductComposition :

N	28.02 %
$P_{25}O_5$	28.16 %
H_2O	1.5 %

Screen size :

over 4 mm	0.2 %
2-4 mm	62.0 %
1-2 mm	37.3 %
under 1 mm	0.5 %

Overall efficiency :

N	98.8 %
$P_{25}O_5$	99.5 %

4. ANALYTICAL CONTROL

Production is monitored by a deviation-correction system (3) which operates on the following premises :

1. A standard deviation, σ , is found experimentally for each fertilizer composition.
2. The maximum acceptable deviation about the nominal composition is assumed to be, in our case, ± 0.2 units.
3. Upper and lower limits are set for those qualities which can be regarded as either acceptable or unacceptable.
4. Sample size is determined.
5. Both attention and correction limits are determined.

The operating procedure consists of taking a number of samples out of which a mean value is obtained. The differences between the actual mean compositions and the nominal concentrations are calculated and added up until a sum surpasses the correction limit; the feed rate is then corrected for that component whose composition is beyond the limit. Once corrected, the computation of cumulative differences starts all over again.

Whenever the sum of differences adds up to the attention limit no correction is effected, but the sampling frequency is increased.

Example for a 6-12-6 NPK :

- Mean standard deviation	0.3
- acceptable deviation	± 0.2
- Nominal composition	6-12-6
- Upper acceptable limit (M_R)	6.2-12.2-6.2
- Lower acceptable limit (M_A)	5.8-11.8-5.8
- Tolerance range ($M_R - M_A$)	0.4

$$\text{- Sample size} \quad n = 3.33 \left[\frac{\sigma}{M_R - M_A} \right]^2 = 1.87 = 2$$

$$\text{- Attention point} \quad h_a = 3.506 \frac{\sigma^2}{n (M_R - M_A)} = 0.40$$

$$\text{- Correction point} \quad h_c = 5.808 \frac{\sigma^2}{n (M_R - M_A)} = 0.65$$

Hence two samples per hour are taken and the differences between their mean values and the nominal compositions (6-12-6) are calculated and added until one of the three sums reaches ± 0.65 , corresponding to the point at which the feed rate for that component is to be altered. The correction is proportional to the percentage deviation.

Figure 2 shows the results of a test run. Points A and B indicate corrections in the feed rates of ammonia and potassium chloride, respectively. In each case the feed rate was decreased by 10%.

The method outlined above allows us to maintain a steady mean production composition within specifications and with remarkably few stray results.

Sample analyses are all automatically carried out by a servoanalyzer capable to measure the concentrations of N (ammonia), N (urea) , P_2O_5 , and K_2O . Each analysis takes about 20 minutes with the analyzer now in use. Samples are taken out of the 1.5-4.0 mm fraction screened out of the dryer's outlet.

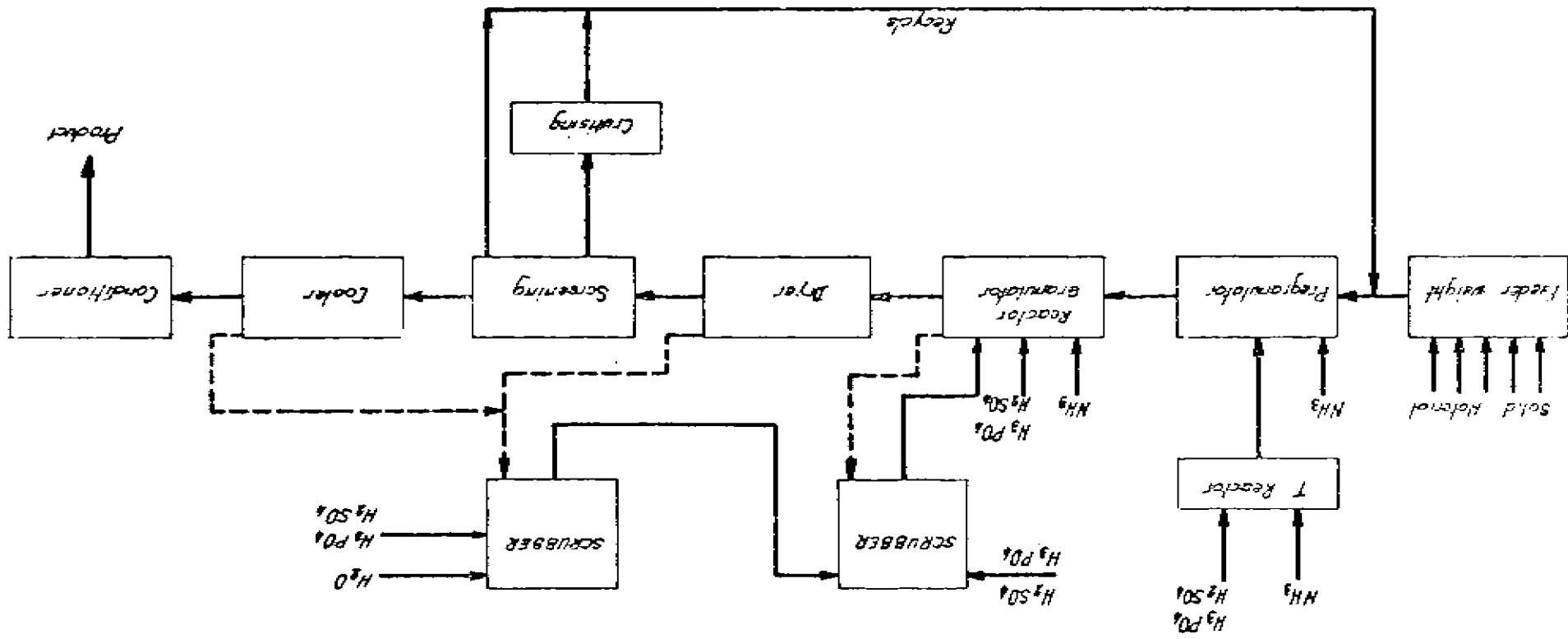
5. PROCESS ECONOMICS

The CROS process offers the possibility of neutralizing all of the sulphuric and/or phosphoric acid within the granulating bed and thus calls neither for additional neutralization units nor for any complex equipment. Production costs are lower in the CROS process on account of the smaller investment required and of the greatly diminished production losses in the intervening manufacturing steps. Another important factor which greatly contributes to decreasing the production cost of high NPK compositions is the possibility of using large quantities of urea and superphosphates (18 %).

Bibliography

1. Lente, R. et al. "Intensive ammoniation in the preparation of granulated complex fertilizers". ISMA LTE/72/12, Seville (Nov. 1972).
2. Frazier, A.W. et al. J. Agr. Food Chem. 95 , 345-347 (1967)
3. Torree-Ibern - The Statistics Methods of Control in the Industrial Process. "Cuadernos de estadística aplicada" 1963 Barcelona.

Fig. 1



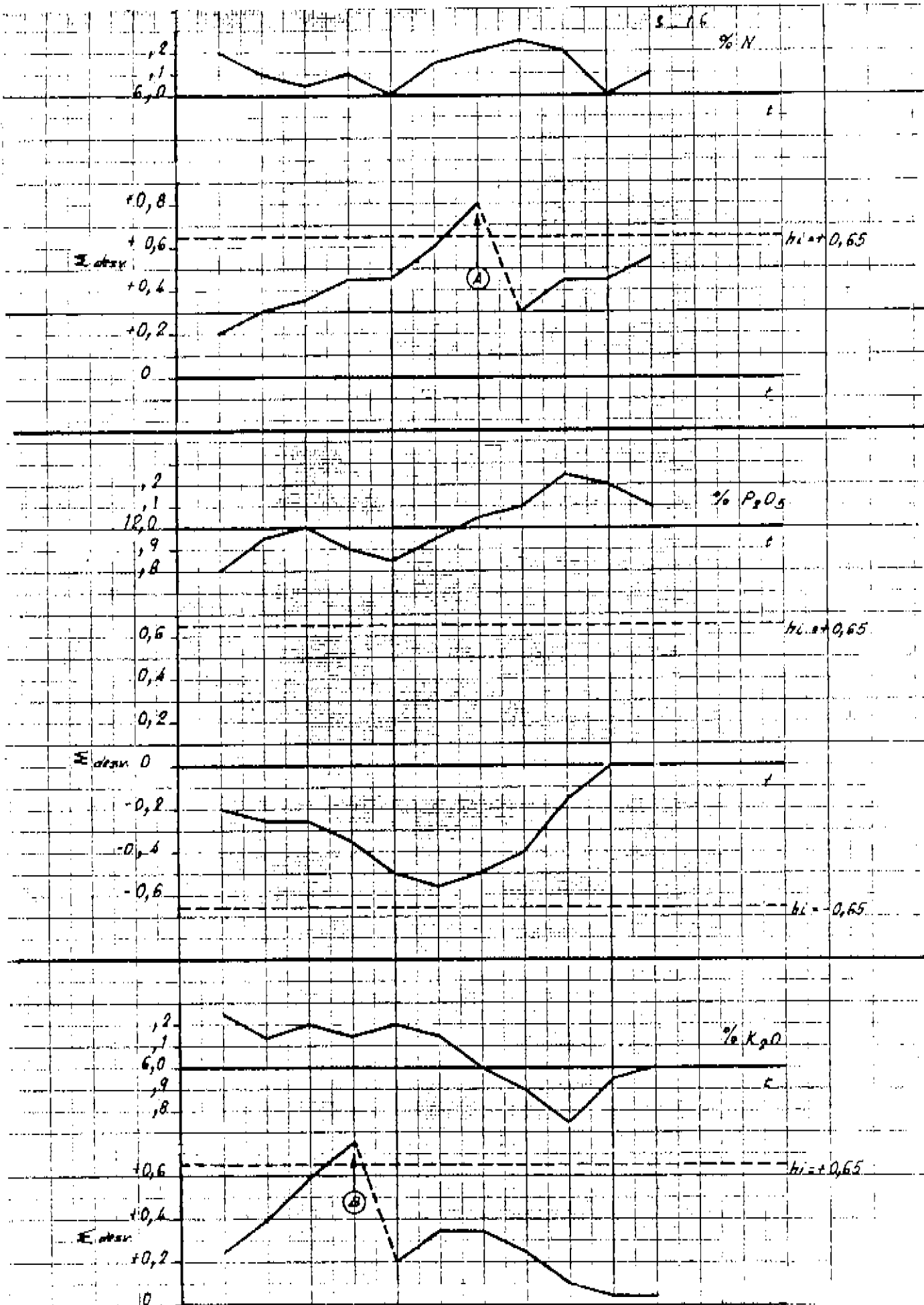


Fig. 2

DISCUSSION

Mr. LOSTE (S.A. Fos, Spain)

Our paper presents some modifications in the conventional flow-sheet and equipment which are used in the manufacture of NPK fertilizers.

We try to achieve the following objectives :

- Simple and versatile process.
- High efficiency in raw materials recovery.
- Less investment for same conventional capacity, diminishing the recycle by improving the granulation performance and more simple ammonia neutralization technology.
- Less emissions to the atmosphere and elimination of liquid effluents by recirculation of scrubber liquors.

The flow-sheet is shown in Fig.1.

The main items which make our process different from conventional ones are :

- Liquid gas preneutralizers are not required. Any intermediate slurry has not to be handled.
- Use of a reactor-granulator in which ammonia neutralization and granulation are carried out at the same time.
- T or pipe reactor for direct reaction between acid (sulphuric, phosphoric or mixture of both) and liquid ammonia.
- Scrubbers and liquid effluents recovery system. Fresh water and acid are used to wash the gases from the reactor-granulator. The resulting solution is used to remove the dust from the drier and cooler. Finally the solution is recycled to the granulator to provide the adequate liquid phase for granulating operation.

The main key points of the process are :

Pregrenulation. This operation takes place in a rotary pan or drum equipped with special ammonia injection equipment.

The following tasks are carried out :

- Low temperature and low humidity pregrenulation in which the granules tend to agglomerate while empty hollows remain.
- Partial ammoniation of the superphosphate. When urea and triple or single superphosphate have to be granulated together, the acid neutralization of these mixtures prevents the formation of an urea-monocalcium phosphate adduct with release of hydration water which could cause excessive overgranulation.

Reaction-granulation. In a rotary drum equipped with special ammonia injection equipment which has been described in an earlier paper, both operations are carried out. Each granule acts like a small individual reactor; the liquid ammonia injected under the bed of solids reacts with the liquid phase supplied on its surface. The temperature increase which results from the exothermic reaction, causes water evaporation and solids deposit. The granulation is achieved through a "layering" process.

A tubular reactor for direct neutralization of sulphuric and phosphoric acid with ammonia is provided to achieve increased ammonia feed rate (in formulations of about 100 kg/NH₃/ton or MAP, DAP urea-sulphate manufacture). The resulting acid slurry is poured on the prgranulator.

Gas scrubbing : All gases from the granulator and the dryer are washed in Venturi type scrubbers. The flow of water required is very low. The water balance is not altered and so, no liquid effluents appear.

Analytical control. Sample analyses are all automatically carried out in a servoanalyser capable to measure the concentration of N in all its forms, P₂O₅ and K₂O. Each analysis takes about 20 minutes. Samples are taken out of the 1.5/4.0 mm fraction screened out of the dryer's output. The production is monitored by a deviation-correction system which operates under the conventional statistics methods of control.

Raw materials. The process is chiefly designed to use : Ammonia and urea, as principal N suppliers, acids effluents, H₃PO₄ acid, triple and single superphosphate as P₂O₅ carriers, conventional K₂O salts.

Materials as ammonium sulphate, ammonium nitrate, MAP or DAP can be used successfully.

The NPK manufacture with urea and superphosphate mixtures requires a special condition treatment to avoid "caking".

Tables 1 to 4 show the results obtained in production runs for several NPK formulations, DAP or NP 28-28. As different features from conventional routes, we can see : lower recycle, liquid effluent system, co-granulation condition for urea and T.S.P. and S.P.

The CROS process offers the possibility of neutralizing all sulphuric and/or phosphoric acid within the granulation equipment, without recourse to any neutralization units. As lower recycle is needed, smaller dryer and additional equipment is required. That causes less investment costs.

Mr. J.D.C. HEMSLEY (Chemical Construction Ltd., U.K.)

Any contribution which is concerned with the efficient recovery of fertilizer materials, and product quality, of considerable value at the present time, and it is well that there are other papers to be given at this conference which are also concerned with this topics. The paper by Dr. BLUMRICH and his co-authors on phosphoric acid technology, and that by Dr. KLIMECEK on the recovery of sulphur from sulphuric acid plant waste gases are notable examples amongst several. As an aside Mr. Chairman, it is perhaps disappointing that our agricultural colleagues do not appear to be so vigorously concerned about the efficient use of fertilisers.

Whilst the technologist is striving to gain a few tenths of a per cent on the maximum utilization of raw materials, we have the situation where five or ten per cent of fertiliser urea can be lost to the atmosphere after application to the soil. But perhaps this is a topic for another conference !

The paper describes a granulation system of two stages which are physically separated. Most other granulation processes use only a single stage for the humidification, neutralization, ammoniation and granulation steps.

I suspect that this has a traditional background, and it is disappointing that the paper does not describe in any detail the mechanical design of the reactor/granulator internal equipment.

The importance of sulphuric or phosphoric acid as a granulation aid, and as a means of reducing the load on the drying stage, has only recently been appreciated in Europe, although such practice has been well known in the USA for more than 20 years.

Mr. LOSTE's paper does well to highlight this technology. The paper also emphasizes the ease with which fertilizers containing high levels of superphosphate and urea can be manufactured in conventional granulation plants.

There has been much doubt expressed in the past about the viability of this system, and the authors must be congratulated in resolving the problems convincingly.

As to the analytical control aspect, we might have some reservations. The statistics used are those intended to provide warning and corrective action levels in a system where the tolerance range is large compared with the normal standard deviation inherent in the system. There seems therefore to be some ambiguity as the quoted tolerance is ± 0.2 , whilst the standard deviation is 0.3.

I have only one question: "What is the storage life of fertilizers manufactured by the Croe process? It seems to me that the relatively high water contents quoted - i.e. - 2.4 per cent - are rather high for a shelf life of more than a few weeks".

Mr. LOSTE

First I'd like to describe in detail the reactor-granulator which we described in Seville in the meeting. We use a small pipe reactor we have inside the pregranulator or inside the granulator. The reactor is covered with teflon. Thus the reaction takes place between acid and ammonia and the acid slurry is poured on the bed. At the same time, liquid ammonia is injected by a special design under the bed along the drum. There are at least 7 or 8 injectors which inject liquid ammonia. It is very important that the ammonia arrives in the reactor in liquid state. We must be sure that we compress the ammonia and so that it arrives directly in liquid state and at the same time, that the ammonia is divided along the reactor. Really when Mr. HEMSLEY said that we use a process in two stages, it is true and I think when urea and single or triple superphosphate are used it is fundamental because it is necessary to neutralize the free acidity of the triple and single superphosphate very quickly to avoid that the reaction between urea and the calcium salt forms an adduct. This adduct releases a big quantity of water and this quantity of water delays granulation. That is the reason why, if urea is used, this prereactor is necessary.

About the analysis control, of course the tolerance is a function of of the market and the law. If you increase the number of samples and the tolerance we can adjust the production to any limit.

About the conditioner it is true. I can give you some data about the caking because I think it is one of the questions we have studied in detail. When 15-15-15 is manufactured using MAP or single superphosphate with urea, there is no difference in the caking effect but when we substitute the potassium sulphate by potassium chloride the caking effect increases. Urea, from the caking point of view, is very convenient to granulate with potassium sulphate, but of course, this would produce a more expensive material. Then we can say that the combination of potassium chloride and urea is responsible for caking. About the water content we saw that it is necessary to decrease the water content to one limit about 1.5-1.8. Less would be convenient but the effect which we get does not justify the higher investment that would be necessary in dryer and cooler and similar equipment. Then we have adopted a conditioner system which consists, in the case of urea fertilisers, of treating the material after we have cooled as much as possible at least under 30°C with a mixture of fuel oil and amine; the amine content in the final material is about 0.03 and the mixture of fuel oil and amine is about 1%. After that a treatment with kieselguhr is advisable. We can say that if the caking problem is very severe it is very advisable to dissolve in the fuel oil a paraffine which solidifies when the material is in storage; then this paraffine protects the granule against caking. I can say that it is very important to test the type of amine which is necessary to use. I have here in my table 4 different materials. Of course I cannot give you publicly the materials, but I advise you to test the different amines before choosing one to make the conditioner operational. We can say finally that in the area based material the conditioning is one of the most important operations to have success. About the time of storage, our experience is more than 6 months. There is no conditioner, there is no material which ensures that the material will be free flowing but we can say roughly a cooling under 30°, water between 1-2% and a conditioner treatment with fuel oil with amine, fuel oil with paraffine and kieselguhr treatment are sufficient.

Mr. NOWAK (Union of Inorganic Chemistry, Poland)

Is it possible according the CROS process to make NPK fertilisers with a formulation 17-17-17 or 1-1-1 based on such inlet material as liquid ammonia, urea, calcined phosphate and potassium chloride and have you tried to manufacture this type of fertiliser ?

Mr. LOSTE

Yes, it is possible to manufacture NPK with 1-1-1 ratio, using liquid ammonia, phosphoric acid, urea, and potassium chloride. Of course according to the ratio, it would be necessary to introduce a filler to adjust the composition, using urea, liquid ammonia, phosphoric acid and potassium chloride to manufacture a 1-1-1 ratio as 17-17-17; only to adjust the desired degree it would be necessary to use some filler to have low P_2O_5 raw material as triple or single superphosphate or MAP if you like to combine them. For instance I can tell you different formulations afterwards where you can say

that 15-15-15 is possible to reach from a combination of MAP, urea and liquid ammonia or a combination with triple superphosphate, urea and liquid ammonia or a combination of DAP etc, only it is necessary to combine the raw materials to reach the final grade.

Dr. BONS (Gewerkschaft Victor, GFR)

I would like to ask a question regarding the P_2O_5 content. An overall efficiency of more than 99% was given here for NPK fertilizers. In many countries we do not reckon in terms of total P_2O_5 but of P_2O_5 with a certain type of solubility. It would be interesting to know which kind of solubility you use in that process for the P_2O_5 . Is it citrate, neutral citrate solubility, etc.?

Mr. LOSTE

In Spain, the agricultural law controls the total solubility, water + ammonium citrate; it is clear that the more you introduce superphosphate in the formulation the more water solubility is decreased. Then I can give you such data for different formulations about the water solubility with our process. In a 15-15-15 with urea where we used single superphosphate about 60 kg/t only as a filler the available P_2O_5 was 99.8 and the water soluble P_2O_5 was 95.1; in one formulation 12-25-12 without urea where we used 100 kg/t of single superphosphate the available water P_2O_5 + ammonium citrate was 99.0 and the water soluble was 80%; in one formulation 10-10-10 with urea where we used 400 kg single superphosphate per ton, the available P_2O_5 was 98% of the total and the water soluble was 63. I think that with these data it is clear that if you introduce single superphosphate of course the water solubility is reduced. If you want all the P_2O_5 as water soluble you can use MAP or triple superphosphate and you have to remove the single superphosphate from all your formulations but of course in the countries where the agricultural law is that the available P_2O_5 would be the P_2O_5 water soluble + ammonium citrate you can introduce as much as possible single superphosphate as you want.

Mr. DEJ (U.K.F. Netherlands)

In table 3 you make DAP with a T reactor, the mole ratio N: P_2O_5 is less than 1. Why did you ammoniate till mole ratio 1, have you any experience with higher mole ratio? and my second question is: the P_2O_5 concentration is 45% in your phosphoric acid. Is that the maximum you have reached?

Mr. LOSTE

I understood that if the ratio N: P_2O_5 in the tubular reactor was more than 1 in the first step, really till now, we prefer to keep the ratio at about this value. We have no interest to increase the ratio in the tubular reactor because we want to neutralize in the granulator as much P_2O_5 as possible to get more heat and remove more water to have less recycle. The philosophy in our process is to neutralize as much as possible ammonia in the granulator because in this reactor if there are small granules and the water is evaporated and is carried out of the system, then the water balance is better and

less recycle is necessary. About the second question the P_2O_5 concentration in the phosphoric acid is controlled for the water balance in the system.

Mr. FROCHEN (COFAZ, France)

In the CROS plant there are three ammonia injectors (3 ammonia inlets), 2 sulphuric acid inlets and 2 phosphoric acid inlets. I fear this means a lot of adjustments to be made at the same time and it should not be easy to operate that plant. Second question can you use more or less warm urea solution or not ?

Mr. LOSTE

Really, we have only one ammonia injection or 2 in the granulator. When we need to prepare DAP, we substitute a standard liquid gas neutralizer handling a slurry with a pipe reactor and in this case, I think our process is better than others because we don't need to handle the slurries. I must say that we did not experience in industrial scale the use of urea in solution but we have had runs in pilot scale manufacturing urea, sulphate, granulator material using a hot solution of urea but our experience is in pilot scale. I don't see now any point to use urea in solution, because the water balance we want will be altered because the water increases with the urea solution will be very very low; then I think it would be possible but our experience is only in the pilot scale.