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SLURRY AMMONIATION IN COMPLEX FERTILIZERS PRODUCTION.  
A NEW TYPE OF HIGH EFFICIENCY AMMONIATOR.

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1) FOREWORD

One of the stages of complex fertilizers production is the neutralization of acid solutions, mainly phosphoric acid, and/or slurries obtained by acid digestion of phosphate rock with ammonia.

Ammonia absorption in this stage raises many problems, and particularly:

1.1) Vapors development: Each kg of absorbed ammonia develops 1 + 2 kg of water vapours. The vapours dilute the gaseous ammonia and the absorption becomes uneasy, especially when the liquid phase is near to neutrality.

1.2) Slurry viscosity. Slurries, particularly in diammonium phosphate production, or from nitric attack of rocks, which contain Ca and other impurities, are viscous, that viscosity coming mainly from precipitated solids. Because of such viscosity, it is very hard and expensive to obtain a pushed neutralization: the difficulty of distributing ammonia in the slurry, during absorbing stages, is added to the difficulty of dilution by vapours under 1.1.

Furthermore, pushed neutralization causes solubility

reduction, and problems become more and more difficult.

1.3) Reactors' size. To avoid too big operating reactors, especially in nitrophosphate production, the ammoniation stage usually consists in many small reactors, connected in series. Such connection leads to the unfavourable consequence of intermediate salts precipitation (monoammonium phosphate; monocalcium, or however little-basic phosphates of Ca in the case of nitrophosphates) which makes a pushed neutralization very uneasy, causing, when Ca is contained in the slurry, insoluble phosphates precipitation. Further phenomena of increased viscosity happen, particularly when rocks rich of  $Al_2O_3$ ;  $Fe_2O_3$ ; MgO are used, and in correspondence with some pH-values: slurry can become unbearably thick, making a good stirring impossible.

When using one reactor in ammoniation of nitrophosphate slurries, it is possible to avoid such troubles, but specific ammoniating capacity is lowered and ammonia losses increase. Furthermore with one big reactor it is difficult to overdo, and sometimes only reach the formation of mono-basic phosphates, because of bigger and bigger problems of viscosity and stirring, when increasing the geometrical size.

## 2. NEW TYPE OF AMMONIA ABSORBER.

Montedison Company, which is producing fertilizers both based on phosphoric acid, and on nitrophosphate process, studied such problem, and succeeded in making up a new type of slurry ammoniator. Such apparatus is based on the principle of separating, the ammonia absorption phenomenon from the one of steam development.

This system, which has been patented by Montedison, presents the following advantages:

2.1) Strong increase of absorption rate of ammonia which

is absorbed under pressure and without being diluted by water vapours.

2.2) Subsequent separation of water vapour in a flash evaporator in absence of free ammonia, and therefore with ammonia losses practically even to those corresponding to the  $\text{NH}_3$ -liquid's partial vapour pressure.

2.3) Washing of ammonia vapours contained in water vapours, in absence of air and therefore with possibility to carry out a complete condensation of effluents.

The basic flow sheet of this apparatus is shown in fig. 1.

### 3) FIRST EXPERIMENTAL STAGE

In 1973, at the Porto Empedocle Montedison factory, a first test apparatus has been built up for the production of ammonia phosphates, which showed to have a practical capacity of 2 t/h of ammonia.

Using such ammoniation, starting from w.p. phosphoric acid it has been possible to obtain an ammonium phosphate slurry containing 11% of water and having a titrimetric neutralization degree  $\frac{[\text{NH}_3]}{[\text{H}_3\text{PO}_4]} = 1,75$ , and analytically  $\approx 1,8$ .

Such value is very much bigger than the one (usually 1,4-1,5) obtained in classical stirred ammoniators.

Going out ammonia from flash evaporator was very low, from 5 to 10% of fed ammonia, in excellent agreement with the one calculated from ammonia vapour pressure diagrams (see fig. 2):

Doing so, we took into account that the neutralization degree 1,75 is the one of a suspension of DAP crystals having  $\frac{[\text{NH}_3]}{[\text{H}_3\text{PO}_4]} = 2$  in a liquid phase neutralized up to a value of 1,5-1,6.

In such conditions, in fact, ammonia vapour pressure of neutralized solutions at 110-120°C, is in the interval of 20 to 60 Torr, and ammonia losses come in this range out.

In the table 1 some operational data are shown: they were obtained during the setting up of phosphoric acid ammoniation, in different conditions of water content and of neutralization degree; checked ammonia losses and ammonia partial vapour pressure, from literature data, are also pointed out.

Market did not require Diammonium Phosphate. It was notwithstanding possible to carry out a test production of diammonium phosphate, starting from w.p. at 42%  $P_2O_5$ , trying to reduce the recycle to minimum value.

Being the amount of ammonia fed to the drum granulation very limited, we could reach a lower granulation temperature - five degrees less.

A recycle ratio from 4 to 4,5 was obtained, optimizing the running parameters, starting from slurries having 12%  $H_2O$  and a neutralization degree = 1,7. When operating with classical apparatuses, the recycle ratio was never less than 6 ÷ 7 times.

This test apparatus has been working two years producing many fertilizers, mainly 20.20.0 and 12.18.12 S.

20.20.0 was made using urea and ammonium sulphate. Urea and a fraction of ammonium sulphate were added to the DAP slurry and the second fraction of A.S. was added to the granulation step; when producing 12.18.12 S,  $K_2SO_4$  only was added during the granulation step.

Recycle ratio was always not more than 4 ÷ 5 times against 6 ÷ 7 times when using classical apparatuses, for both 20.20.0 and 12.18.12 S; reduction was chiefly connected with the reduced heat quantity developed in granulation step because of the reduced quantity of ammonia.

TABLE 1 - Wet Process phosphoric acid ammoniation. Test carried out at Porto Empdocle

Test N°	Ammonia: kg/h	Slurry %H <sub>2</sub> O	Slurry Temp. °C	Titrimetric degree of neutralization		going out smokes m <sup>3</sup> /h	evaporated water kg/h	going out ammonia kg/h	Ammonia vapour	pressure from	yeild of absorbed NH <sub>3</sub> %
				slurry	liquid calculated				diagrams Torr	measured losses Torr	
1	1,800	16.0	119	1.6	1.48	10,000	2,500	131	34	42,5	92,5
2	1,750	30.0	108	1.78	1.78	14,000	2,500	390	150	122	78
3	1,750	13.0	113	1.8	1.6	7,000	2,500	163	55	59	90,5
4	1,750	12.5	112	1.8	1.58	6,500	2,500	213	44	64	88
5	1,450	17.4	114	1.71	1.59	26,000	2,000	104	60	37	93
6	1,500	21.6	118	1.66	1.6	24,000	2,100	132	65	48	91
7	1,800	17.9	121	1.58	1.52	23,000	2,500	134	42	40	93,5
8	2,000	20.6	116	1.65	1.58	23,000	2,800	117	55	32	94
9	1,530	11.0	115	1.75	1.51	23,000	2,100	81	34	30	94,5
10	1,600	15.2	116	1.68	1.51	23,000	2,300	67	34	21	96
11	1,500	25.3	110	1.69	1.69	22,000	2,100	71	85	26	95
12	1,400	12.5	115	1.66	1.47	22,000	1,950	71	24	26	95
13	1,750	13.8	117	1.45	1.45	26,000	2,500	57	23	19	96,5

The going out ammonia being very low during both slurry and drum ammoniation steps, two further advantages set out: it was never necessary to use diluted phosphoric acid for ammonia recovery, but acid 40 + 42% was always used without problems of precipitation; ammonia losses have shown insignificant: less than 0,2 + 0,3% of total amount of fed ammonia.

#### 4) SECOND EXPERIMENTAL STAGE

Following the good results obtained with the test apparatus of Porto Empedocle it was decided to fit up a second new-type ammoniator at Porto Marghera by an existing plant for phospho-nitric attack of rock, the capacity of which was 700 to 1.000 tons fertilizer per day. This plant is fitted out with a classical drum granulator-ammoniator, a dryer, screening and crushing facilities.

This second ammoniator, built using makeshift apparatuses showed an absorbing capacity of 5 t/h of ammonia.

The following grades have been produced after fitting up:

20.20.0	from $H_3PO_4$ , $H_2SO_4$ , Ammonium Sulphate and small quantities of $HNO_3$
20.10.5 S	from $H_3PO_4$ , A.S., small quantity of $HNO_3$ and Potassium Sulphate.
8.24.24 S	} from phosphoric attack of rock
12.18.12	
11.22.16 S	
25.10.0	

During the production of 20.20.0 and 20.10.0 S the same problems regarding phosphoric acid ammoniation set up. Slurries very easily treatable, having 10%  $H_2O$  and a titrimetric neutralization degree of  $P_2O_5 = 1,75$  were obtained.

The amount of ammonia fed to the granulation drum, which was before up to 1.200 kg/h was cut down to 0 to 300 kg/h, with remarkable advantage in granulation step, where temperature was lowered of about 5 to 10°C.

The bottle-neck removal both in slurry and solid stages, and chiefly the different chemical and physical characteristics of slurries, made it possible a capacity increasing from the former 650-700 t/day to present 1000 t/day. Going out ammonia, reduced to 5 to 7% of fed ammonia, has been very easily recovered in the gas-absorbers. Ammonia losses, after absorbers were practically nul.

Table 2 shows the operational conditions before and after the new ammoniator fitting up.

The production of fertilizers from phosphonitric attack of rock raised quite a different set of problems. If ammoniation is carried out in traditional way, that is in a series of reactors, the following phenomena happen:

4.1) Development of NO and N<sub>2</sub>O during first neutralizing step

4.2) A viscosity increasing with pH up to a maximum for pH = 3 to 4 (corresponding to monobasic phosphates) and afterwards a reduction for higher pH values (see diagram fig. 3)

4.3) Insoluble salts of P<sub>2</sub>O<sub>5</sub> precipitation, particularly if Fe-rich rocks are used (ferric-ammonium phosphate) at pH in the range of 1,5 to 2,5

4.4) Insoluble Ca phosphate formation for pH-values exceeding 4-4,5

To minimize such drawbacks, chiefly with concentrated and Fe-rich slurries, the best way was:

The nitric attack slurry was rapidly ammoniated using two reactors settled in parallel, up to a pH of 2 to 2,5, to reduce the nitrogen oxides losses. The w.p. phosphoric acid was separately ammoniated to pH 5 to 5,5.



T A B L E 2

parameters	units	20 - 20 - 0		20-10-55 + 10S	
		traditional ammoniation	high effi- ciency ammo- niation	traditional ammoniation	high effi- ciency ammo- niation
capacity	ton/h	29	37	26	40
ammoniation degree of slurry		1.1	1.75	1.3	1.5
NH <sub>3</sub> granulator drum	Kg/h	950	0	500	200
	kg/ton	33	0	19	5
Recycle ratio		7.5	5,8	7,7	4
Recovered NH <sub>3</sub> from slurry ammoniation	kg/h	100	300	65	100
Losses of NH <sub>3</sub>	kg/h	3.5	0.5	1.3	0.2
Temperature	°C	75	68	85	82

Both slurries were mixed together, obtaining a slurry; the neutralization degree (of soluble  $P_2O_5$ ) of which never exceeded the value of 1; doing so, both viscosity increasing and insoluble Ca phosphates precipitation were avoided.

By using the new type ammoniator such difficulties were wholly cut down, because it is possible to reach in one step the final conditions of neutralized slurry. The running becomes easier, being intermediate pH-values control unnecessary.

The problem of insoluble phosphates precipitation is cut down too, also in correspondence of a very high neutralization degree, that is 1,7 to 1,8 on water soluble  $P_2O_5$ .

This advantage comes from the fact that, operating in one stage only, also for a high neutralization degree, intermediate precipitation of little-neutralized salts, that make it hard to reach final equilibria, does not happen and local conditions of liquid over-ammoniation never occur.

Some little troubles happened after the new ammoniation, such as some casual blocking of pipes and pumps. The cause if these troubles must be debited to the makeshift installation, particularly in the connections with the other parts of the plant where the new ammoniator was fit up.

The possibility to have a slurry ammoniation without danger of thickening and of  $P_2O_5$  losses, gives the advantage to check up the most favourable conditions for high capacity. This side is now in stage of refining: it has been seen that for very pushed neutralization degrees an over-granulation tendency occurs: the problem is to find out the fittest conditions, for best results.

According to the results obtained up to this moment and without looking for mechanical systems to avoid the overgranulation, the best way to run the granulation is that one of ammoniating the slurry till a neutralization degree immediately before the high-viscosity field, sending the remaining

ammonia to the drum granulator. In such a condition it has already been found the possibility of a capacity increase of about 10% in comparison to the capacity of the classical multi-reactors flow-sheet; physical properties of product were also improved.

It is possible to consider that by mechanically operating on granulation step and particularly on granulator and on slurry feeding and distribution, it is possible to reach still better results.

The present trend is to carry out tests in such a trend.

Ammonia going out from the ammoniation was very low for nitrophosphates too: less than 10% of fed ammonia: no problem therefore arose for its high yield recovery, also having at disposal little amount of phosphoric acid.

The possibility of obtaining high neutralization degree, also during ammoniation of nitrophosphate slurries, makes it possible to get advantages also concerning the self-sustaining combustion of final fertilizer. This phenomenon is in fact tied to the neutralization degree of product, and becomes null in correspondence of a pushed neutralization degree. Fig. 4 shows the horizontal combustion rate plotted against the  $N_{amm}/N_{nitr}$  ratio for a 15-15-15 phosphonitric fertilizer. Such combustion rate becomes = 0 for  $N_{amm}/N_{nitr} = 1,8$  corresponding to a neutralization degree = 1,8.

Another useful advantage rising up from that new type of ammoniator is an increased stream factor of a plant. In fact every change of grade required, using traditional apparatuses 8 to 18 hours of plant stopping, chiefly in function of analogy between the two grades. Using the new type ammoniator, stopping time is halved on an average because of the cleaning speed, and the changing of the slurry phase being easier.

The second advantage during grades changing, is the possibility of reaching more shortly the full capacity of production from starting-up. That's particularly useful when the market requests many grades, and frequent grades changes are necessary.

## 5) TECHNICAL PROSPECTS

Remarkable possibilities can be foreseen for the appliances of the new type of ammoniator for both new and existing plants, considering what described above.

The peculiar conception of this apparatus offers the following technical advantages:

5.1) Slurry viscosity is much less conditioning

5.2) Ammonia losses are lined up with the slurries' ammonia vapour pressures.

5.3) Gaseous effluents from flash evaporator do not contain inerts

5.4) Geometrical problems for apparatuses scale-up are minimum

5.5) Problems for intermediate precipitation do not exist

The following consequences can be derived:

5.6) A capacity limit for a single unit does not exist: it is possible to conceive single units for absorbing 30 t/h and more  $\text{NH}_3$ ; in fact we can conceive no limit for pumps, for flash evaporators and for raw materials inlets.

5.7) Problems of gaseous effluents abatement, particularly ammonia are reduced to a minimum in comparison to those relevant the classical system.

5.8) It is the apparatus which links together the ad-

vantages of absorbing stage under pressure and of effluents developments at atmospheric pressure.

5.9) It is the apparatus that links together the most favourable conditions of slurry concentration and of neutralization degree with the maximum of ammoniating elasticity.

5.10) An investment cost reduction and higher plant elasticity for different grades ensue for new plants.

5.11) The possibility of capacity increasing linked to a wider range of obtainable grades and to a reduction of environmental problems because of lower losses, ensues for existing plants.

Other interesting prospects, different and presumably more profitable than those coming from a coupling with a classical drum granulation plant are envisaged for the future.

The future trend of research is directed towards a binding to a granulation systems, where granulation and drying are carried out together, without necessity of neutralization in solid phase.

The new type of ammoniator appears to be particularly fit for that type of plants.

Plants, where granulation and drying are carried out together usually where a slurry is sprayed out against a solid granular product rapidly moving, exist already.

In the Priolo Montedison factory a fluidized bed granulation plant has been working many years, where the drying gas enters at  $400 + 450^{\circ}\text{C}$ , and where diammonium phosphate 18-46-0 from diluted phosphoric acid and other granular fertilizers are produced.

It can be deemed that a coupling of a high efficiency slurry ammoniator to such a plant will be able to open interesting prospects towards plant simplicity and installation costs, towards elasticity and quality of product, and with

possibility of minimizing environmental problems, chiefly if working with high concentration and neutralization degrees.

The program is to carry some tests out as soon as possible.

Montedison is now planning to supply some of its plants with new industrial ammoniators, with the collaboration of Tecnimont which is the engineering firm of Montedison Group.

It was not yet planned to carry out some tests in the field of polyphosphates. The possibility of dealing with very viscous slurries, and of pushing the ammoniation degree opens prospects also in this field, which shows very promising.

As far as the economics are concerned, it is very difficult to say something, the possible applications being too many.

Information about installation costs, running costs, and performances, can be supplied by Montedison-DIPA - Milano or by Tecnimont - Milano.

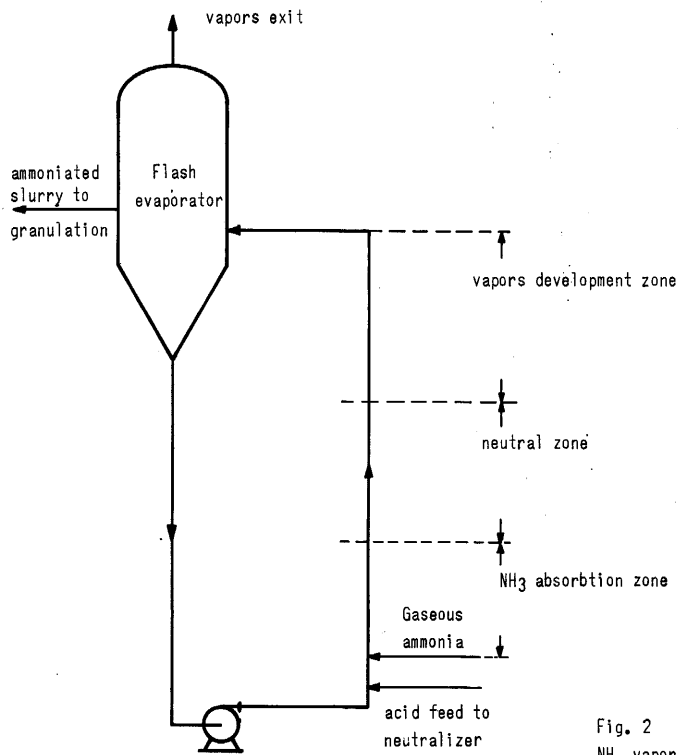


Fig. 1 - High efficiency ammoniator basic flow diagram

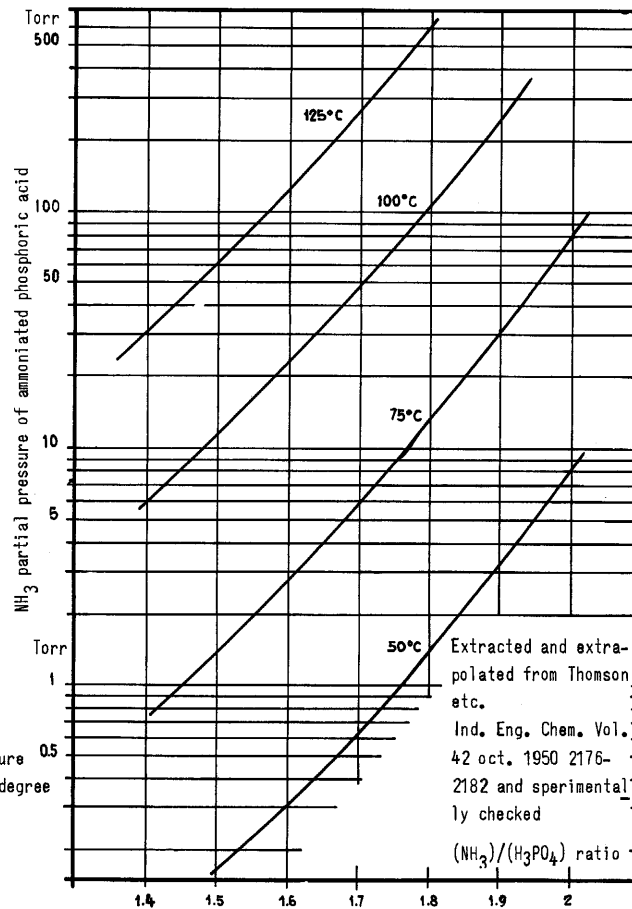


Fig. 2  
 $\text{NH}_3$  vapor pressure vs ammoniation degree of w.p.p.a.

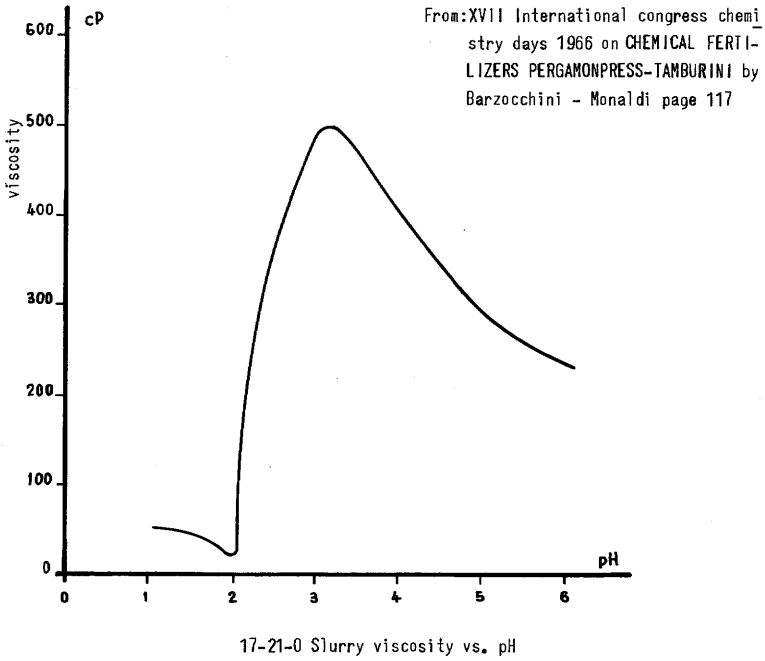


Fig. 3

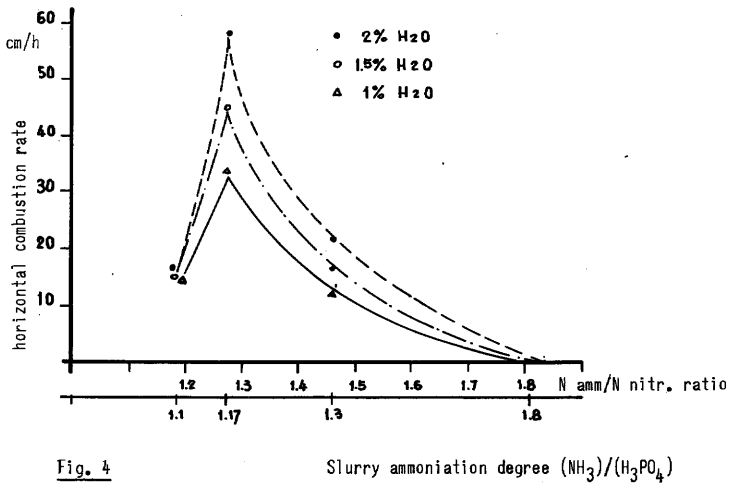


Fig. 4