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EVALUATION OF PRODUCTION FLEXIBILITY AND COSTS BY NPK PILOT PLANT EXPERIMENTATION

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1. INTRODUCTION

The general fertilizer production routes have now been standardized and it seems unlikely that any particularly innovative technology will emerge in this field. Consequently the companies involved that have pilot plants use them to improve existing processes from both the economical and technological point of view. From the technological point of view attempts are being made to improve process recoveries and to make emissions comply with the ecological laws that are becoming progressively more stringent. From the point of view of savings, cheaper raw materials and more economical formulations are being tested. The pilot plants are also used to produce large samples of new products for both quality and agronomic tests. Pilot plants exist in various sizes, from the semi industrial to that of the laboratory. Considering the two extremes of the range it can be said that semi-industrial pilot plants supply very reliable elements for the realization of larger plants and allow thorough studies to be made of innovative technologies. They are however at least as expensive to construct, maintain and operate as an industrial plant. On the other hand small pilot plants on the laboratory scale do not supply sufficiently valid scaling up criteria but they have the advantage of costing less and requiring lower operation costs.

EniChem Agricoltura was formed by the merging of two companies and therefore the processes used are based on different technologies. In fact two plants carry out phosphate rock attack with sulphuric, phosphoric and nitric acid while another does not attack the phosphate rock but feeds phosphoric acid. Also the granulation techonologies vary from plant to plant:

- Drum granulator
- Spherodizers
- Spouted bed

This permits not only great flexibility in obtaining many different grades of fertilizer but also leads to greater complications on the production level. It is therefore more important for EniChem than for other producers with more standardized technologies to use the pilot plant before carrying out industrial trials. For these reasons we decided to build a pilot plant with a continuous cycle on laboratory scale. After five years of operation of this plant (even if in a discontinuous manner) it can be concluded that the choice was economically justified and several million dollars have been saved on the industrial plant.

2. PILOT PLANT DESCRIPTION

The plant was completed in 1987 and cost, in its final version, half a million dollars. It is normally kept in operation 16 hours a day for two shifts with two people per shift. Normal running conditions are attained in about three hours and it takes three hours in the evening for the shut down and the cleaning operations. Therefore it can run continuously for a total of about ten hours per day with the production capacity of 20 to 50 kg/h. The hold up of the plant is about 50 to 60 kg depending on the production cycle used.

It is composed of a liquid section for the production of:

- slurry for NPK
- melted urea from prilled urea.
- 90% ammonium nitrate from ammonia and nitric acid.

An approximate flow sheet of the liquid cycle is given in Figure 1.
Basically it is constituted by four reactors in series for the phosphate rock attack, neutralization with ammonia and dissolution of the potash salts.

Furthermore it is equipped with feeders for liquid and solid raw materials and gaseous ammonia. The volume of each reactor is about 30 liters and its stirring power is about 0.5 kw.

With minor modifications to the salt cycle granulation can take place with all the technologies now being used in the industrial plant.

The various components of the plant are described in Figures 2 ,3 ,4 and 5.

Despite the very compact lay-out, the small pieces of equipment (0.6 m diameter the granulator, 3.5 m long the drier) lose a considerable amount of heat and therefore the plant has been fitted with a secondary fan that feeds hot air into the equipment to minimize thermal dispersion.

The granulator can be modified in its internals to obtain the "falling curtain" necessary for granulating urea. The drier can function both as a drier and as a spherodizer with no particular modification.

It is extremely simple to change from one technology to another and it takes only a few hours to carry out the modifications.

3. WORK CARRIED OUT IN THE PILOT PLANT

3.1 Production of fertilizers from nitric acid attack of the phosphate rock with a higher content of water soluble P_20_5

In the plants with a spouted bed or spherodizer cycle the slurry is always neutralized to the pH of the finished product due to the impossibility of neutralizing in solid phase.

Furthermore, it must contain all the salts of the finished product since raw materials cannot be fed during the granulation phase.

With these conditions it can be difficult to obtain high values of the fraction of the water soluble P_20_5 if certain operating criteria are not respected, particularly:

- H+/Ca0 and $S0_4$/Ca0 ratio in the attack phase,
- number of neutralization stages to control the slurry viscosity,
- control of the impurities in the raw materials.

Normally, during the phosphate rock attack, sulphate ions are added to precipitate the calcium as calcium sulphate in order to raise the water soluble P_20_5 content in the final product.

The normal temperature of the attack is about 60°C to avoid the distillation of nitric acid.

At this temperature, using ammonium sulphate or potassium sulphate as the source of $S0_4^=$, the calcium precipitates as dihydrate calcium sulphate. By neutralizing with ammonia boiling temperatures are reached, the sulphate of calcium bihydrate is no longer stable and turns into hemihydrate sulphate of calcium with another crystalline habitus that puts the calcium ions into solution again.

It is therefore necessary to carry out the neutralization in two stages:

- a sufficiently acidic stage whose conditions do not cause the calcium phosphate to precipitate because of an absence of HPO_4 = ions. In this step the calcium precipitates again as hemihydrate stable phase.
- a more neutral stage in which the ammonia reacts with the water soluble P_2O_5 to produce only ammonium phosphates.

If, on the other hand, neutralization occurs in the presence of dihydrate calcium sulphate insoluble P_2O_5 can form. Furthermore ammonium sulphate forms giving double salts with the ammonium nitrate (sulfonitrates) increasing the caking tendency of the finished product. The study of the crystalline phases, through the separation of the precipitates in each reactor, and the successive chemical and X-ray analyses were carried out in the pilot plant operating continuously. All the plant sections were operated to control also the quality of the finished product and a formulation was found with a desired percentage of water soluble P_2O_5 (see Table 1 for the compound 15.15.15).

3.2 Development of low pH formulation

The lowering of the pH in products to limit ammonia losses in the driers has been a common tendency in all the plants over the past few years.
Fertilizers with a $N/P_2O_5 > 1$ ratio are rich in ammonium nitrate and this predominant salt makes the solubility of their slurry insensitive to pH variations.

For those products with a low N/P_2O_5 ratio (1/3 as for example, in compound 8.24.24) where it's not possible to feed ammonium nitrate this operation proved more difficult since the solubility of the ammonium phosphates is sensitive to the pH (Figure 6) and, consequently, the pH of the slurry cannot be chosen freely.

An attempt in the plant to gradually decrease the granulation pH from the previous value of 5.8 to the value of minimum ammonia losses did not give positive results because of the instability of recycle size. The availability of the pilot plant allowed considerable variations to be carried out on the formulation without the problems of producing tons of sub-standard product.

In this way it was possible to determine the optimum granulating conditions which were found to be very different from those normally used, as can be seen in Table 2.
With the product obtained in the pilot plant it was also possible to carry out tests to find an anticaking agent resisting the acidity of the substrate.

3.3 Use of the granular MAP as intermediate

A study carried out in the pilot plant which had considerable immediate economical consequences was that on the use of the granular MAP on the spherodizer plants.
This raw ~~material, very interesting from the economical point of view,~~ was used directly in the industrial plant substituting more expensive phosphoric acid. An immediate drop in the water soluble P_2O_5 was noticed which could not be explained by the chemical characteristics of the MAP used. The slurry characteristics in the pilot plants test procution of 15.15.15 with granular MAP are shown in Table 3.

Various hypotheses were tested in the pilot plant without the production of thousands of tons of sub-standard product. The reason for the drop in water soluble P_2O_5 as found to be the imperfect dissolution of the granular MAP which was fed in the neutralization stage whose liquid phase was consequently poor in phosphate ions. The problem was solved by introducing the granular MAP directly in the attack phase to allow its complete dissolution and attain a correct CaO/P_2O_5 ratio.

3.4 Granular potassium sulphate

The possibility of producing granular potassium sulphate in the complex fertilizer plant of Priolo was studied in the pilot plant.

Normally granular potassium sulphate is obtained through the compacting on rollers of very fine powders.

In this way a granulation is obtained even if the physical- mechanical characteristics of the products are poor.

Since this process cannot be transferred to the existing plants it was decided that the equipment would be adapted to accomodate the material.

It is known that the potassium sulphate is only slightly soluble in H_20 and it is therefore impossible to make solutions sufficiently concentrated to granulate properly.

A process was therefore developed which, while not being exactly optimum, nevertheless allowed the objective to be reached without any particular expenditure.

In particular, the production of potassium sulphate suspension was developed in such a way as to obtain homogeneous slurry with a high content of suspended salts. A bentonite of national origin which maintains the salt in suspension even with a water content of only 30% was used. The slurry thus obtained was granulated in a drum with a classical granulation cycle and additional potassium sulphate was fed directly into the solid in order to raise the production rate.

The mechanical resistance of the finished product depends strictly on the residual humidity of the granules. At less than 1.5% humidity the resulting product of the pilot plant was of the same quality as that of the commercially available product.

Because of production exigencies the K_20 concentration must be limited to 47%.

The operating parameters are illustrated in Table 4.

Table 1 Slurry characteristics in the pilot plant test production of 15.15.15. with spherodizer.

Parameters	Units	Attack and CaO precipitation	First Neutral. reactor	Second Neutral. reactor	Potash Mixing reactor
Temperature	°C	60	112	116	90
pH	-	-	2.5	6.3	6.2
moisture methanol extr	%w	27	23.7	21.5	20.6
<u>Dry basis composition</u>					
NITROGEN					
Ammoniacal	%	7.8	10.6	13.3	10.2
Nitric	%	8.8	7.7	7.3	5.6
Total	%	16.6	17.7	20.6	15.8
P_2O_5					
Water soluble	%	22.3	20.3	17.9	12.6
Citrate	%	22.4	21.4	20.8	15.2
Insoluble	%	0.1	0.1	0.3	0.3
K_2O	%	-	-	-	15.2
CaO	%	8.2	8.2	8.1	6.4
SO_4	%	11.0	11.0	10.7	8.4
<u>X rays composition</u>					
$(NH_4)_2HPO_4$	%	0	0	0	8.8
$NH_4H_2PO_4$	%	0	48.5	30.0	0
$CaSO_4 \cdot 1/2H_2O$	%	7.6	39.7	24.8	10.2
$CaSO_4 \cdot 2H_2O$	%	33.4	0	0	0
$(NH_4)_2SO_4$	%	0	0	0	0
NH_4Cl	%	0	0	0	10.0
$(K,NH_4)H_2PO_4$	%	0	0	0	22.9
KNO_3	%	0	0	0	22.7
KCl	%	0	0	0	1.1

Table 2: Comparison of operating parameters between low pH and high pH 8.24.24.

Parameters	Units	Low pH values	High pH values
Production rate	t/day	960	960
<u>Raw materials</u>			
NH_3	Kg/t	73.5	83.9
HNO_3	Kg/t	102.0	71.6
Morocco rock	Kg/t	129.8	121.7
P_2O_5 from H_3PO_4	Kg/t	200.6	203.2
H_2SO_4	Kg/t	0	37.2
KCl	Kg/t	397	397
<u>Finished product</u>			
pH	-	4.0	5.8
N ammoniacal	%	5.8	6.5
N nitric	%	2.2	1.5
water soluble P_2O_5	%	18.0	18.0
citric P_2O_5	%	24.0	24.0
K_2O	%	24.0	24.0
<u>Slurry</u>			
moisture	%	15.0	18.0
pH	-	2.5	2.5
<u>Granulation</u>			
recycle rate	t/h	160	200
product moisture	%	3.0 to 3.2	3.5 to 4.0
pH	-	3.5 to 4.0	5.8 to 6.2
temperature	°C	95	100
<u>Drying</u>			
air temperature	°C	250	300
product moisture	%	1.0	1.5
product temperature	°C	95	100

Table 3. Slurry characteristics in the pilot plant test production of 15.15.15. with granular MAP.

Parameters	Units	Values for the final slurry
Dry basis composition		
NITROGEN		
Ammoniacal	%w	10.3
Nitric	%w	4.8
Total	%w	15.1
P_2O_5		
Water soluble	%w	10.7
Citric	%w	13.7
Insoluble	%w	2.1
K_2O	%w	15.4
CaO	%w	6.4
SO_4	%w	9.6
X rays composition		
$(NH_4)_2HPO_4$	%w	0
$NH_4H_2PO_4$	%w	0
$CaSO_4 \cdot 1/2H_2O$	%w	0
$(K,NH_4)_2SO_4 \cdot 2(K,NH_4)NO_3$	%w	28.0
NH_4Cl	%w	18.1
$(K,NH_4)H_2PO_4$	%w	12.6
KNO_3	%w	14.8
KCl	%w	1.9

Table 4

Operating parameters during granular K_2SO_4 production

Parameters	Units	Values
PRODUCTION RATE		
of the plant	Kg/h	17
REACTOR ONE		
bentonite	Kg/t	40
water	Kg/t	400
Temperature	°C	40
Permanence time	min	120
REACTOR TWO		
K_2SO_4	Kg/t	700
15% K_2SO_4 solution from stack abatement	Kg/t	150
Temperature	°C	80
Permanence time	min	80
FINAL SLURRY		
moisture	% w	44
Viscosity	cP	20
Shear limit	dyne/cm	15
GRANULATOR		
K_2SO_4	kg/t	200
Recycle ratio	w/w	20
Moisture	%	5.5
Temperature	°C	60
DRYING		
Air temperature	°C	250
Product temperature	°C	60
Product moisture	%	2.5

Fig. 1

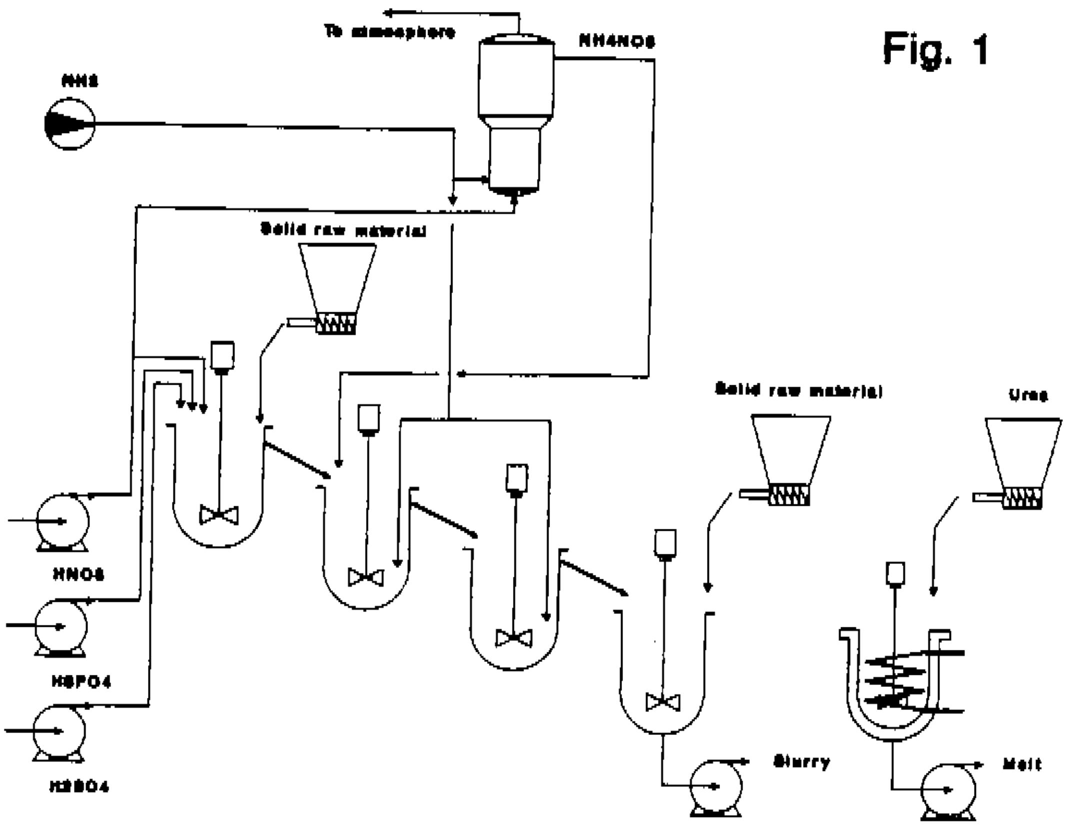

Fig. 2 : drum granulation

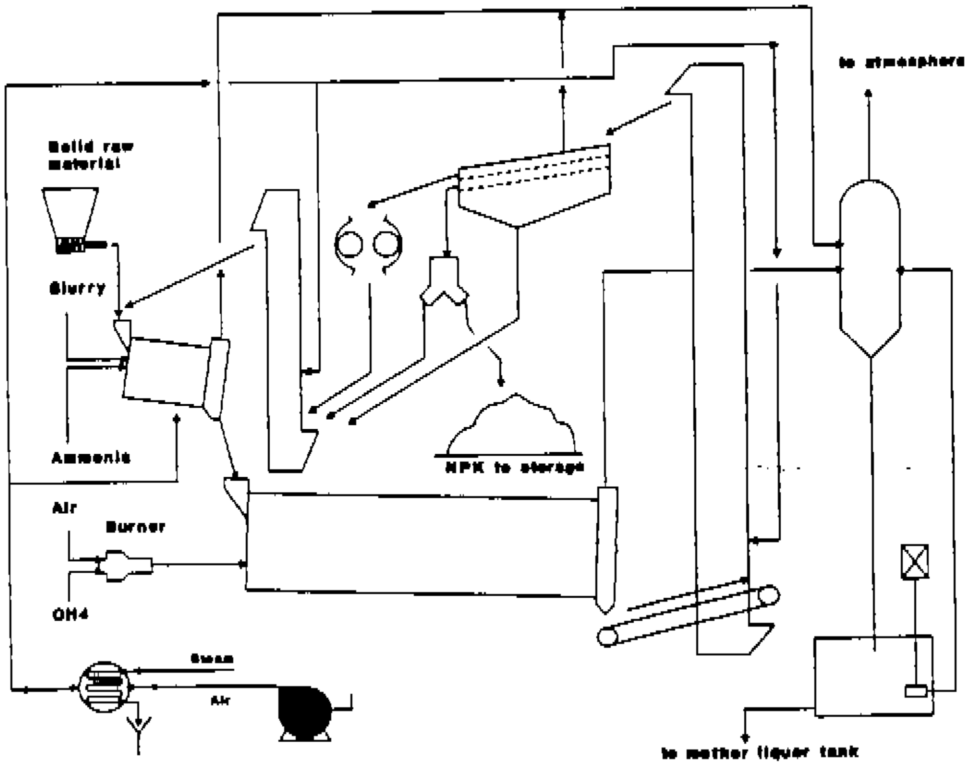

Fig. 3 : spherodizer

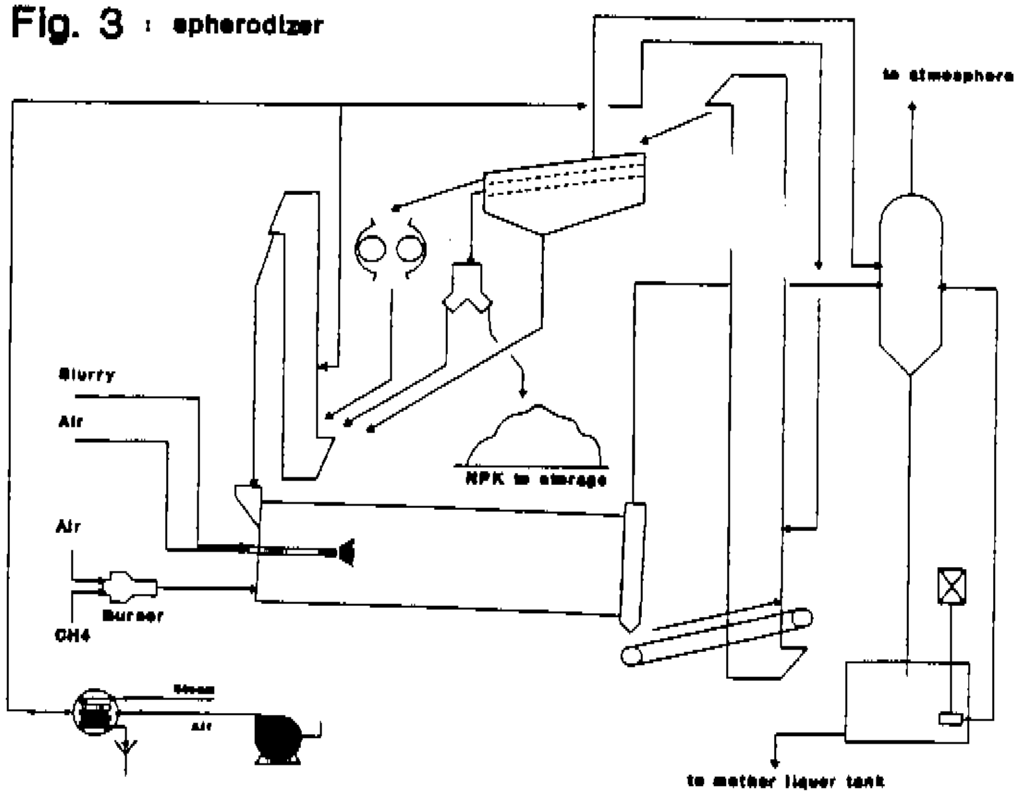

Fig. 4 : falling curtain

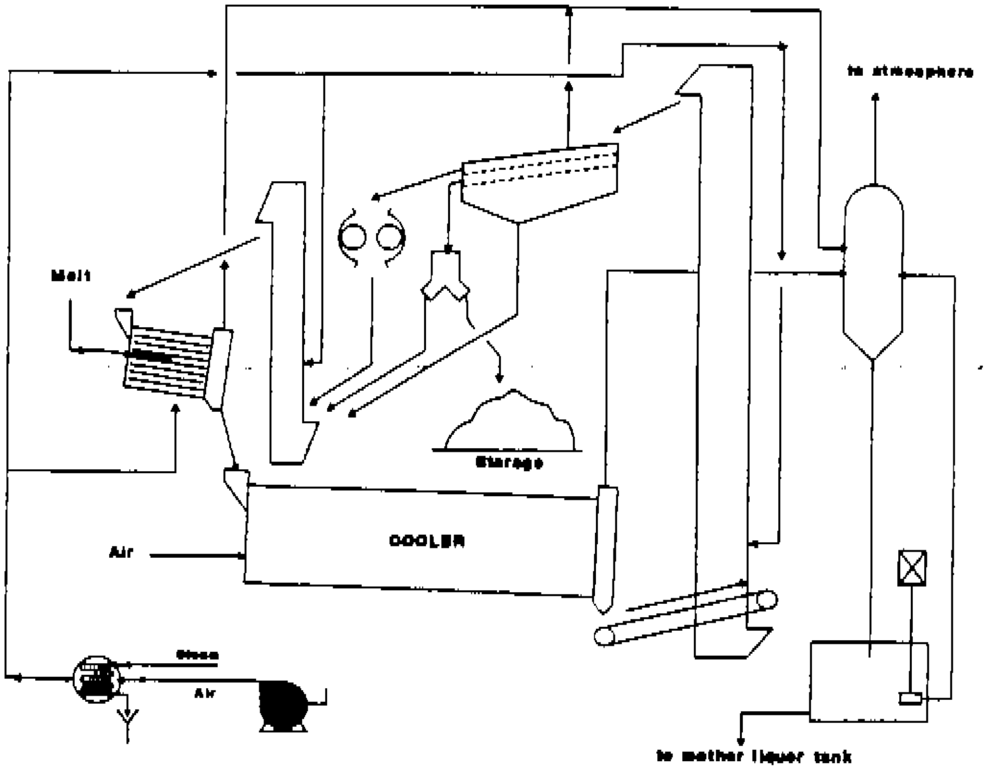

Fig. 5 : spouted bed

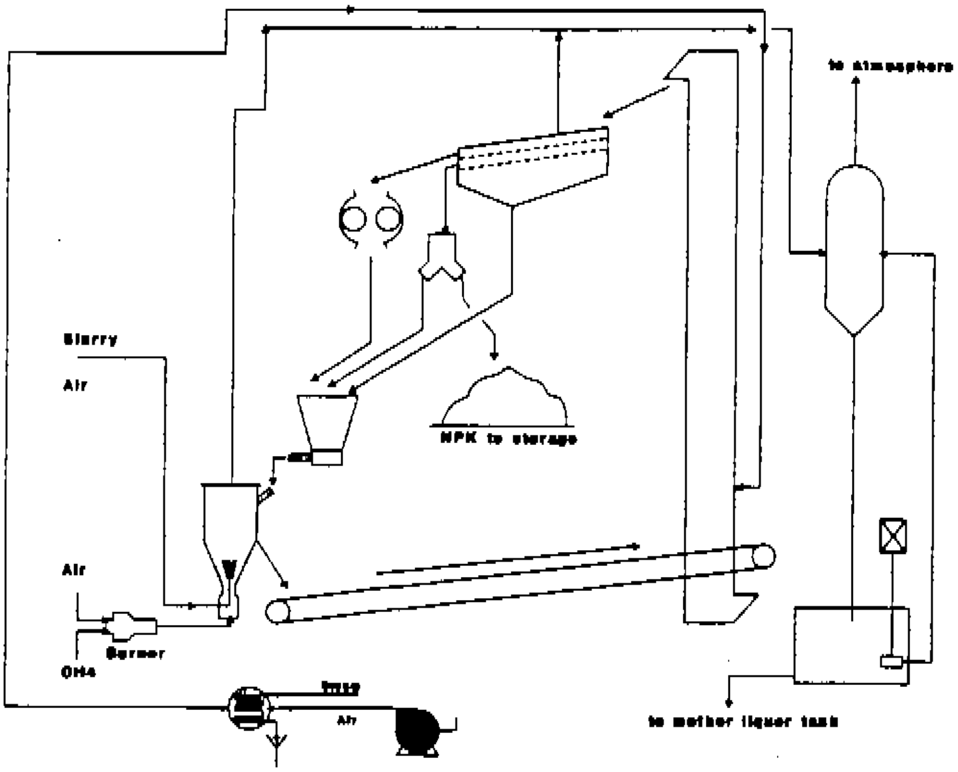

FIG. 6

SOLUBILITY OF THE AMMONIUM PHOSPHATES