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POWDERED OR GRANULAR MAP AND DAP VIA PIPE REACTOR TA/86/9

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## 1. SUMMARY

The ERT-ESPINDESA pipe reactor achieves the reaction of phosphoric acid and ammonia to make MAP or DAP in a single piece of equipment.

Acids from different sources have been used in the manufacture of both MAP and DAP. Even Florida sludge acid has been tested with good results.

The last development is powdered DAP which can economically substitute to the powdered MAP as an intermediate to the manufacture of NPK fertilizer.

## 2. INTRODUCTION

According to this process the manufacture of ammonium phosphates, either powdered or granular, is based on the use of a special reactor of proprietary design which achieves the reaction of ammonia and phosphoric acid up to $NH_3/H_3PO_4$ molar ratios above 2.0 in a single piece of equipment. Ammonia spillage from the reactor is negligible when MAP is produced and amounts to only 10-15% of the feed when DAP is manufactured.

A melt of MAP or DAP mixed with water vapour is produced in the pipe reactor and therefore the manufacture of powdered MAP or DAP is achieved by spraying the melt from the top of a tower or alternatively by spraying it inside a rotary drum in case that granular product is to be produced.

## 3. MAP

Since 1966 the ERT fertilizer complex located at Huelva has been manufacturing powdered MAP, some of which is used in a neighboring NPK granulation plant. The rest is exported by train, truck or ship to other ERT plants in Spain.

The old ERT Minifos plant was retrofitted in 1981 with the pipe reactor to produce 450 Tpd of low moisture powdered MAP.

The process consists of a pipe reactor located at the top of a tower 17 meters high. The pipe reactor is made of stainless steel and is fed with phosphoric acid and ammonia to produce a melt of MAP which solidifies when falling inside the tower (Fig. 1).

The moisture of the product is controlled by adjusting the acid strength of the phosphoric acid fed to the pipe (see Fig. 2) in such a way that for a certain $P_2O_5$ content in the phosphoric acid and a molar ratio $NH_3/H_3PO_4$, a given moisture in the MAP is obtained. Usually the moisture of the product is kept at a level of 4-6% to have a free-flowing product. Lower moisture means dust losses, and higher moisture could cake the product and make transport more expensive. Another factor influencing the caking tendency is the acidity of the product. Low pH increases the chances of caking.

The tower is natural-draft type. The product is collected in the bottom as a powder, at a temperature of 60ºC. It can be stored without caking or directly used as an intermediate in the manufacture of NPK granules.

Ammonia losses are almost negligible and therefore the cooling air from the tower can be scrubbed with phosphoric acid or water, to recover the entrained MAP particles. If phosphoric acid is used as a scrubbing liquor, the acid is used as feed to the pipe reactor. In the case of using water, a part of the water is used to dilute the feed acid.

Features of the system:

- Very simple plant design, i.e. low investment
- Easy operation
- Moisture of MAP can be adjusted from 2% to 12%
- Very high ammonia and $P_2O_5$ efficiencies
- When 44-45% $P_2O_5$ phosphoric acid is used as raw material, the MAP contains 4-5% moisture, which means a saving of steam in the concentration step of phosphoric acid equivalent to 100 kg of steam per each 1% of concentration.

- Acids with high impurities content can be used. As a matter of example we show the results of the test made with sludge acid (bottoms of a Lamella thickener) from Florida rock.

| | |
|---|---|
| $P_2O_5$ | 42.64 |
| CaO | 0.60 |
| $SiO_2$ | 0.11 |
| $Fe_2O_3$ | 3.85 |
| $Al_2O_3$ | 1.84 |
| F | 1.55 |
| $H_2SO_4$ | 5.50 |
| $Na_2O$ | 0.17 |
| $K_2O$ | 0.36 |
| MgO | 0.73 |
| Solids (methanol) | 16.40 |

The analysis of the powdered MAP was the following:

| | |
|---|---|
| Nitrogen | 9.78% |
| $P_2O_5$ water sol | 41.53% |
| $P_2O_5$ citrate sol | 50.75% |
| $P_2O_5$ total | 50.78% |
| $H_2O$ (Karl-Fisher) | 1.94% |
| pH | 4.1 |

## 4. GRANULAR DAP

According to the Fig. 3, fresh phosphoric acid with a concentration of 40-42% $P_2O_5$ is fed to the final gas scrubber. From there it passes to the two-stage ammonia scrubber, where it absorbs most of the ammonia lost in the granulator. From the ammonia scrubber, the partially neutralized phosphoric acid, with an ammonia to phosphoric acid molar ratio of 0.2-0.3, is pumped to the pipe reactor, where it reacts under pressure with ammonia up to a final molar ratio as required to make DAP, usually 1.9-2.05 depending on the impurities present in the acid fed. The reaction is instantaneous and exothermic and most of the water content of the phosphoric acid evaporates to dissipate the heat of the reaction.

On the other hand the heat of the ammonia-free gases leaving the scrubber is used to evaporate the liquid ammonia before being vented to the atmosphere because the ERT-ESPINDESA pipe reactor needs to be fed with gaseous ammonia. Through this system, ammonia is vaporized without the need of using live steam.

From the pipe reactor, the hot concentrated DAP melt is sprayed over recycled DAP in the granulator, which is of the rotary drum type and lined with self-cleaning rubber panels. Due to the low water content of the hot DAP melt, the recycle ratio can be kept between 2.5 and 3.5. At the exit of the drum, the moisture content of the product is below 3.0%. NO AMMONIA IS ADDED DIRECTLY TO THE GRANULATOR. Excess ammonia from the granulator is recovered in the ammonia scrubber as described.

The granules fall directly into a rotary drier where it is dried to the desired moisture content. Product leaving the drier is sent, via a bucket elevator, to the screens, where it is divided into three streams: oversize, product and the fines. The coarse fraction (oversize) is passed to the mill where the crushed material is discharged, together with the fines from the screen, into a recycle bin. The output from this bin is regulated in such a way that a constant feed of material is recycled to the granulator. The on-size material from the screen is conveyed to storage.

Hot air from the drier is removed through cyclones to the gas scrubber before being discharged to the atmosphere.

### 4.1. Features of the system

- Low recycle ratio: 2.5 - 3

- Easy operation (there is only one ammonia feed to the plant, fewer pieces of equipment are required than in conventional processes, no hot slurries are to be pumped, no need for an ammonia sparger in the granulator).

- Lower operating costs

- Lower investment cost (smaller equipment size due to the lower recycle ratio and the simpler lay-out that can be achieved).

- High $P_2O_5$ solubility in water (98% compared to 90-92% for DAP produced in conventional processes with Morocco acid).

- Easy retrofitting to existing DAP plants to increase the production rates up to 50%.

- Acids with high impurities content can be employed as feed-stock.

## 4.2. Raw materials and utilities consumptions for producing granular DAP (18-46-0)

Raw materials consumptions, t/t

| | |
|---|---|
| Ammonia (100% $NH_3$) | 0.221 |
| Phosphoric acid (100% $P_2O_5$) | 0.463 |

Utilities consumptions

| | |
|---|---|
| Steam, kg/t | 1 |
| Electricity, kWh/t | 25 |
| Fuel Oil, kg/t | 2 |

## 4.3. Raw materials and product quality

Phosphoric acid feed analysis:

| | Morocco | Florida |
|---|---|---|
| $P_2O_5$ | 40.15 % | 47.03% |
| F | 1.41 % | 1.45% |
| $SO_3$ | 1.943% | 3.92% |
| $SiO_2$ | 0.47 % | 0.11% |
| CaO | 0.79 % | 0.33% |
| $Al_2O_3$ | 0.434% | 1.73% |
| $Fe_2O_3$ | 0.457% | 2.43% |
| MgO | 0.439% | 0.73% |
| $Na_2O$ | 0.164% | 0.17% |
| $K_2O$ | 0.017% | 0.14% |
| $Cl^-$ | 0.033% | n.a. |
| Org. Mat. | 0.02 % | n.a. |
| Susp. Solids | 2.44 % | 6.50% |

DAP Analysis obtained with those acids

| | | |
|---|---|---|
| N | 18.25% | 17.15-17.93% |
| Water soluble $P_2O_5$ | 45.12% | 41.68-44.47% |
| Citrate soluble $P_2O_5$ | 46.44% | 46.21-49.00% |
| **Total $P_2O_5$** | 46.57% | 46.21-49.03% |

$$\frac{\text{Water sol. } P_2O_5}{\text{Total}} = 96.89\%$$

$$\frac{\text{Water sol. } P_2O_5}{\text{Total}} = 99.72\%$$

Attention should be brought to the high water and citrate solubility of $P_2O_5$ of the DAP produced with this process. No further studies have been done to explain this fact but it seems possible that the short residence time of reactants inside the reactor do not allow $P_2O_5$ to form some of the non-soluble salts which usually appear when making commercial grade DAP. A computer program has been developed to predict the water solubility of the DAP that can be produced from the analysis of the impurities of the acid.

### 4.4. Pipe reactor description

Depending on the phosphoric acid impurities, the pipe-reactor can be made of 316 L SS or Uranus 36. Some of the reactors used at ERT's Huelva works are now in the third year of operation.

Pipe diameter and length are variable according to the design rate. For 25 t/h of DAP the diameter is 4 inches and the length is 20 feet. Only 5 feet are placed inside the granulator.

The pipe-reactor is supported outside the granulator and therefore the retrofitting of an existing granulator is very simple.

Some build-up and blockage of the reactor has been experienced after several days of operation when high magnesium oxide content (above 2.2%) acids have been used. The analysis of the scale shows that some insolubles and hard ammonium magnesium phosphates are formed, containing over 15% of MgO.

The above problem does not exist when low magnesium oxide acids are used.

## 5. POWDERED DAP

In view of the fact that ammonia spillage from the pipe reactor was on the order of 10-15% of the feed when the ammoniation of phosphoric acid was conducted at molar ratios $NH_3/H_3PO_4$ close to 2.0, the idea was developed of producing DAP in a different form: powdered.

On the other hand some of the NPK formulations low in nitrogen (i.e. 8-24-8, 5-15-15, etc.) do not admit only MAP as a source of nitrogen and $P_2O_5$. We came to the conclusion that the ideal situation would be to have a plant able to produce any powdered ammonium phosphate with a molar ratio $NH_3/H_3PO_4$ between 1.0 and 2.0.

The benefits of fixing double amount of ammonia (the cheapest source of nitrogen) to the phosphoric acid and making a product that could be used as ingredient in granulation and fluid fertilizer plants, were clear. In the ERT plants in Spain alone the savings amounted to several million dollars.

In other words, we tried to combined the advantages of powdered MAP and the chemical composition of DAP.

5.1. Pilot plant

A pilot plant was erected consisting of a forced-draft tower provided with a pipe reactor of a capacity of 400 kg/h DAP in a similar way to Fig. 1.

The first trials were conducted with Morocco acid.

After the necessary adjustments, a free flowing powder of DAP was obtained. Moisture of the product was on the order of 6-10% and could be easily varied by adjusting the acid strength of the feed. The water solubility of the product was 97-98%.

By adjusting the acid strength, both the molar ratio and the moisture of the product can be optimized.

The performance of the pilot plant pipe reactor is indentical when producing powdered or granular DAP. The operating conditions are the same.

Senegal acid has also being tested and has given excellent results, quite similar to the Moroccan acid, except for some foaming tendency, which required the addition of antifoaming agents in the scrubbing system.

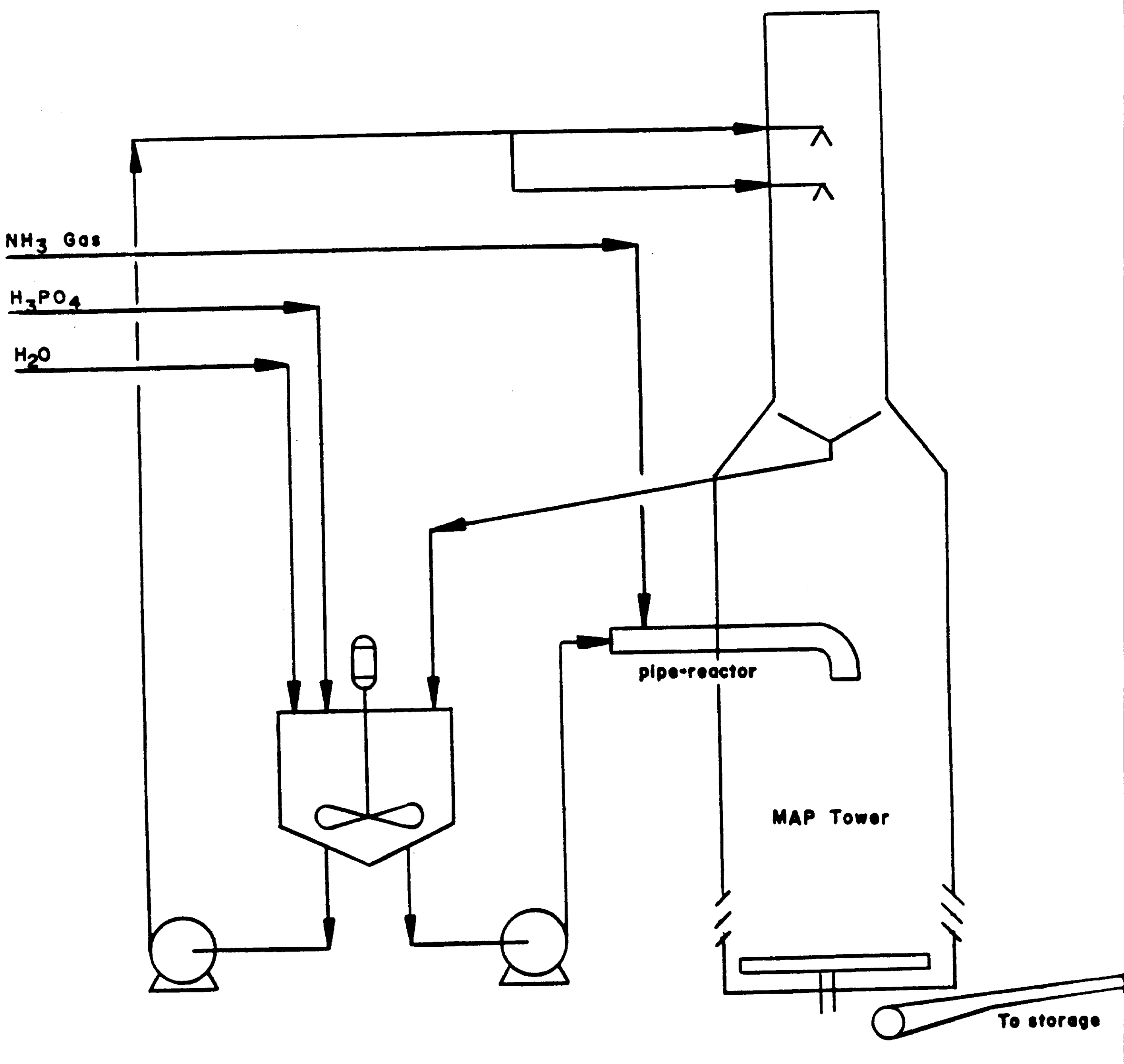


**FIG. 1**

**ERT - ESPINDESA Process for MAP**

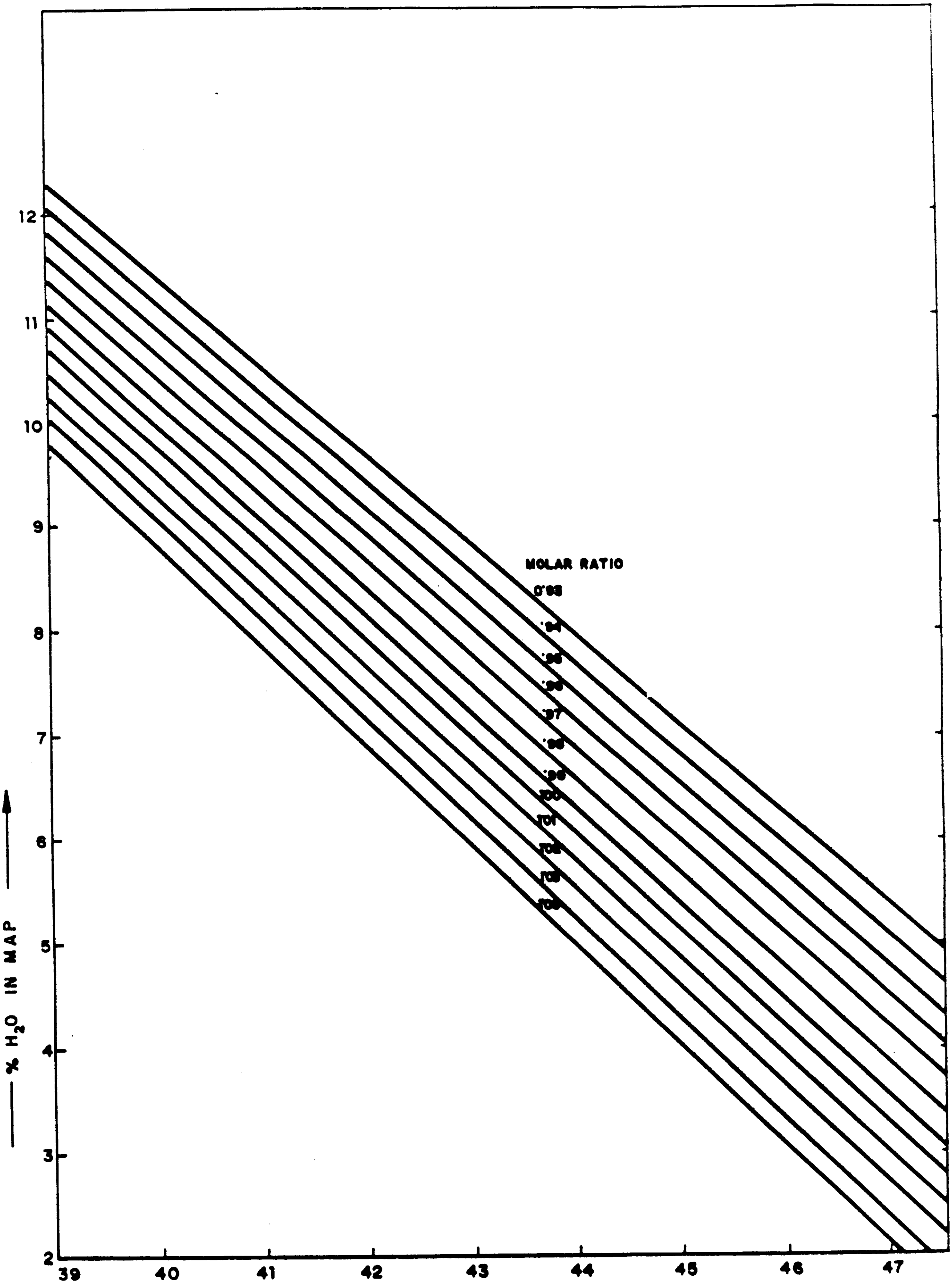


Fig. 2.- MOISTURE OF THE MAP VS $P_2O_5$ CONTENT OF THE ACID FEED.

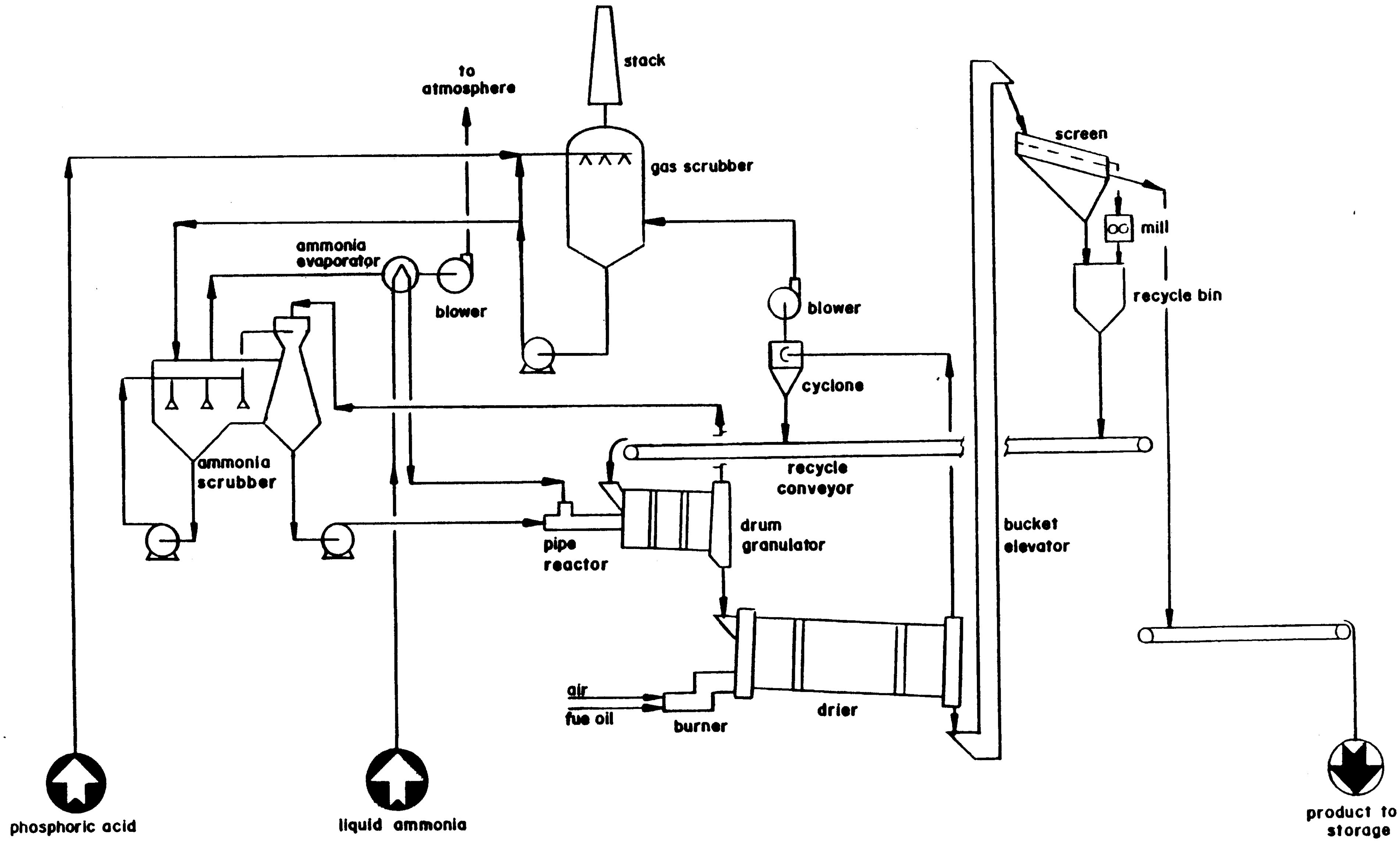


**Fig. 3**

**The ERT — ESPINDESA Low Recycle DAP Process.**

TA/86/9 Powdered or granular MAP and DAP via pipe reactor by
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DISCUSSION : (Rapporteurs Mr A. Constantinidis, SICNG, Greece &
Mr V. Bizzotto, NSM, Netherlands)

Q - Mr D. LEYSHON, Jacobs Eng., USA

What size of pipe reactor is required for large sized DAP plants, say 100 Tph or more and what size of granulator would be used?

A - For 25 Tph of DAP, pipe reactor diameter is 4 inches
For 60 Tph of DAP, pipe reactor diameter is 6 inches
For 100 Tph of DAP, pipe reactor diameter is 8 inches
Granulator size for each capacity is smaller than for conventional processes due to the lower recycle rate and the fact that our granulator has no internals.
We cannot give you, at this moment, size of granulators because, until now, all our references are for plants producing either DAP or NPK based on urea what requires larger size for some equipments than if only DAP should be produced.

Q - What level of ammoniation in product DAP can be produced, as evidenced by final product pH?

A - Product DAP as produced in our process has pH of 7,4 - 7,5 and the ammoniation molar ratio is 1.9 - 2.0.

Q - Mr M. BARLOY, SCPA, France

With your tower process, can you produce powder DAP with 2% moisture? and under what conditions of concentration and molar ratio?

A - Most of our experience in tower has been with 40% P2O5 and molar ratios around 2.0. With those conditions the final moisture varies between 6 and 10% as it is said in the text. Nevertheless, acids up to 42% P2O5 have been used in other tests and moistures of 4% have been achieved, but we have not tried to go below this point because our experience with powder MAP shows that, under 4% moisture, the product becomes too dusty, and we expect the same problem with powder DAP.

Q - Mr P. ORPHANIDES, Duetag, France

What is the main advantage of producing DAP molar ratio 2.0 in the pipe reactor, against the production of MAP/DAP of molar ratio 1.4/1.6 and complete the ammoniation in the granulation bed. Is it just more simple?

A - The main advantage of our process is the low recycle ratio. At the exit of the pipe reactor, the melt contains 6-10% moisture and requires less than 3 parts of recycle (moisture 1-1,5%) to granulate.

Other advantages are the need of only one ammonia feed what implies easy operation control and the fact that the granulator has no internals then avoiding formation of lumps.

Q - Mr T. NURMI, Kemira Oy, Finland

What are fluorine, dust and ammonia emissions to the atmosphere?

A - Fluorine, ammonia and dust emissions do not depend on the process itself but on the scrubbing system design. In regard to emission the process is equivalent to other processes. In some of our plants, ammonia cannot be detected in the stack.

Q - What are the temperature and pressure in the pipe reactor?

A - Temperature is 125-135°C and the pressure 3.5 atmospheres.

Q - Is it possible to use nitric acid, also?

A - Definitely yes.
At present time we are designing an ammonium nitrate plant which includes neutralization of nitric acid by a pipe reactor.

Q - Mr MEZGHANNI, SAEPA, Tunisia

For which purpose does the pipe reactor of your concept use gaseous ammonia instead of liquid ammonia which could avoid the presence of an additional vaporization unit?

A - Our pipe reactor requires ammonia vapour. Anyway we vaporize the ammonia by using the heat content of the gases leaving the granulator.

Q - Mr M.H. JENNEKENS, DSM, Netherlands

For a typical industrial unit using the pipe reactor for DAP production, what size of rotary drier do you expect?

A - The product leaves the granulator containing 2.5-3% moisture. The size of the drier depends on the final moisture required. Anyway, as the recycle ratio is only 3, the amount of solids to be dried is lower than in conventional processes and therefore the dryer size should be smaller.