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PROJECT FOR PHOSPHORUS COMPLEX AT MORON

Caracas, 18/01/88

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CONTENT

1. Scope of work
2. Rehabilitation of existing phosphoric acid plant and new plant
3. Capacity expansion of existing NPK/DAP plant (pipe reactor and/or MAP plant) and new plant
4. Conclusions and Recommendations

1. SCOPE OF WORK

- A. Conceptualization of project on fertilizers, specifically in the area of phosphates.
- B. Determination of technical feasibility to increase the capacity of existing plants.
- C. Up to date knowledge of available technologies and licensors available in the market.

With respect to A. concentrations have been given to:

- global definition of project development in the area of fertilizers containing phosphates
- identification and analysis of alternatives
- technical feasibility of increasing the capacity of existing plant

2. REHABILITATION OF EXISTING PHOSPHORIC ACID PLANT AND NEW PLANT

Rehabilitation of existing phosphoric acid plant is in progress and some work on site have been started already. Design for rehabilitation and changes have been done on the basis of the previous experience of PEQUIVEN's engineers, when operating the plant on Riecito rock. Dihydrate Dorr Oliver process is modified in such a way that deblockenecked will be part of the equipment according to the characteristic of Dorr Oliver process and Riecito Rock. This should be done when this plant was designed at first time.

Number of licensors which are offering dihydrate process (see enclosure 2) means that they have developed their process by modified type of the equipment, sizes, materials, etc. according to the characteristic of certain number of raw phosphate. It means that if even one of "simple" dihydrate process will be chosen for new phosphoric acid plant it will be necessary during the contractual stage and design stage to check each part of the equipment if it could perform the foreseen duty according to the characteristic of Riecito rock. Unfortunately when according to Master Plan contract for the new phosphoric acid plant should be signed will not be known results how successful are modifications made on existing phosphoric acid unit according to the process parameters. Main concern for the decision of the capacity for the new plant is what will be the capacity of the existing phosphoric acid plant when starting after rehabilitation made. Limitation for the capacity of the existing plant based on Riecito rock is surface of filter area, which could not be changed. From previous experience there is not data what was the maximum daily capacity limited by filter area because of the problems on equipment before filter. After rehabilitation done it is expected that all problems on equipment will be minimized and achieved process performances as designed in first place. Therefore it is to recommend that all changes on the equipment for the existing phosphoric acid plant would be taken in the account, when choosing the technology and equipment for the new phosphoric acid plant. Especially will be valuable calculations for the new sizes of equipment based on the characteristic of Riecito rock and spare taken on existing plant according to the capacity of filter, because it is fundamental difference between plants in nitrogen complex and phosphorus complex. In nitrogen complex when defined process for certain plant nearly all have been

defined. For plants in phosphorus complex such as phosphoric acid and DAP/NPK each part of process should be separately tailored together with the choice of process technology. For example following should be considered for each process under consideration as main parts of process for phosphoric acid production.

Rock grinding

Throw the surface of rock reaction with sulphuric acid take place. It is intention to create sufficient free and large pore surface area to allow complete dissolution of the rock in a relatively short period of time together with minimizing power requirements for agitation. The first problem is to specify the style, size and the number of grinding units together with power requirements necessary. The second problem is the optimization according to the operational problem characterized by the chosen process which require certain rock feed, size distribution, power etc. to achieve an economic balance for the plant as a whole. High degree of flexibility should also be provided to accommodate changes in rock supplies.

For Riecito rock and for flexibility of using imported rock grinding equipment should be chosen among usually used for dry grinding process.

The Reaction System

Phosphate rock, sulphuric acid and recycle acid have to be feed regularly and with accuracy into the reaction tank to keep reaction conditions as constant as possible. Investment in quality equipment in the raw material feeding systems quickly pays off by avoiding disturbances in regular crystal growth, losses by coating and co-crystallization, variable filtration characteristics of the gypsum cake etc.

The reactor as a key equipment of producing phosphoric acid uses many different designs. The size of the reactor has to be large enough to:

- provide sufficient retention time for the phosphate rock to be completely converted
- provide enough reaction or retention time for regular crystal growth and adequate crystal size
- permit breaking of foam and emulsion of the slurry during and after the reaction section

Design of reactor to process as many as possible of Riecito rock deposit should be defined together with the licensor on the base of experience on different type of phosphates.

The Filtration System

Separation of phosphoric acid from calcium sulphate crystals should be as complete as possible. Surface of the filter area should correspond to the quantity of recycle

acid which is double filtered. The risk of loss of P2O5 is increased and the quality of filtration is very important specially when operating with low-grade rock or processes producing more concentrated acids directly. Consequently the risk of losing P2O5 due to the occasional upset of the filtration system may invalidate the theoretical advantages of certain processes, when fed with lower grades of rock. This apply to Riecito rock also because this deposit could go rather low in P2O5 content.

Filter area is limited factor for achieved capacity for certain phosphate, but little could be get by increasing the speed of rotation. Therefore it is better to have a sufficient safety margin incorporated in the filter area.

The filter including acid and vacuum piping and pumping, represents about 50% of the investment cost of a phosphoric acid dihydrate plant and choosing the filter type is of major importance. Selection criteria is based on following:

- capacity, function of surface and speed
- total investment costs, including filtration equipment, vacuum pumps, acid pumps, piping, instrumentation, and civil work.
- water consumption
- maintenance costs, including filter cloth consumption
- maintenance costs, including filter cloth consumption
- corrosion and reliability

Acid Concentration Systems

The concentration operation to the required P2O5 grade acid is accomplished by evaporation under vacuum, normally using the by-product steam generated during sulphuric acid production as a source of energy produced in the quantity more than sufficient to satisfy the needs of phosphoric acid concentration.

According to the capacity of process reactor first should be decided to built one or two concentration units and than single-stage or multistage. For Riecito acid seems that the most efficient sludge removal will be through an intermediate 40% P2O5 concentration.

Next to be choosen is type of heat exchanges and material of construction by considering the following:

- high heat transfer coefficient
- low scaling
- little corrosion and erosion
- sufficient mechanical resistance

If fluosilicic acid is recuperated system for washing the gases should avoid contamination with P2O5.

The next very important influence on the process parameters will be from the differences in the quality of Block A, B and C of Riecito rock analysed by Dorr Oliver. For example, when Gafsa rock fall down for 2% in quantity of P2O5 it was necessary to add additional tank to improve process parameters but even with this, strength of acid decreases for 2% (see enclosure 2). In the case of Riecito rock there are the differences in the quantity of P2O5 up to 10% with great differences in the quantities of impurities. This could lead that will be even impossible to process all quantity of Riecito rock deposit. But for sure will be rather difficult to get guarantees for process parameters from licensors based on this differences in the quality of the Riecito rock. When the licensors will know complete analyses of Riecito rock deposit they may not require sample for testing because non sample could apply on total deposit. This also make almost impossible to choose technologies with hemihydrate process route such as hemihydrate process (HH) or hemidihydrate process (HDH) because hemihydrate route require very stable quality in the phosphate rock. If in the meantime will be received offer for the new phosphoric acid plant based on hemihydrate route this must be entirely examine for acceptance.

The problems how to choose the process for new phosphoric acid plant has been well recognised by International Fertilizer Development Center (IFDC) what could be seen from their offer to make study by testing Riecito rock on their bench scale pilot plant (400 Kgs of rock). IFDC do not expect to get any valuable result by testing of Riecito rock and they put main accent in the offer on their contacts with licensors on behalf of Pequiven. Because every licensor will be reluctant to work with Pequiven throw any institution, they do not expect to get reliable process data from licensors what could get Pequiven, if directly approach licensors. Therefore IFDC offer to provide for Pequiven from licensors only what is normal part of each contract between licensor and technology buyer.

Training of Intevep people to operate pilot plant testing facilities installed in Venezuela has theoretical value and could be partly used for testing other phosphate deposits in Venezuela to get some data before approaching licensors.

Still remain main concern: How to choose the process for the new phosphoric acid plant?. First of all to choose the process is not Pequiven's obligation but licensor's responsibility. Each preference to some of processes could be checked when received the offers from licensors.

Pequiven's obligation in the meantime is to give the base to licensors and thus enable them to choose the process. It seems rather uncertain to choose the process based on the quality of Riecito rock deposit. Risk is even greater if phosphoric acid plant is considered as a part of the whole project. What to do if phosphoric acid plant will not produce? To import acid is too many and if will be imported DAP than DAP/NPK could not work and sulphuric acid should lower the capacity. Other approach to the problem of Riecito rock quality is how to lower its influence on the working condition of the plant. This could be possible if it is acceptable that phosphoric acid plant is working PART TIME ON IMPORTED RAW PHOSPHATE having following advantages:

- this will increase capacity on both phosphoric acid plants for more than 30%.
- maximum possible use of Riecito rock
- abrasion on equipment will reach acceptable level per tone of P₂O₅ produced before replacement required

Suggested base for choosing the process on the flexibility of buying different phosphates on the market have similarity in the differences in quality from different phosphate with the differences in quality in Riecito deposit but lower expressed. On this way type, size and material for equipment chosen will allow to use most of Riecito deposit having sometimes differences in capacity what could be compensated by working part time on imported raw phosphate.

The base for choosing the process for the new phosphoric acid plant will be then:

Capacity:

- 500 MT/D based on Riecito rock
- Possible use of other phosphates

Proposed licensors for fulfill above requirements will be:

- Norsk Hydro, UK
- Prayon, Belgium
- Rhone Poulenc, France

3. CAPACITY EXPANSION OF EXISTING NPK/DAP PLANT (PIPE REACTOR AND/OR MAP PLANT) AND NEW PLANT

A. OPERATION CHARACTERISTIC OF EXISTING DAP/NPK PLANT

Existing NPK/DAP plant have capacity when producing DAP from 700-1000 TPD (according to the concentration of phosphoric acid used) and NPK from 900-1200 TPD (according to the grade produced and quality of raw materials used).

Production on existing NPK/DAP plant is characterized by slurry route used maximum of recycle ratio when producing DAP and NPK grades. This mean that operators are using plant capacity at maximum possible rate based on slurry route and this gives them plenty of maintenance work to keep the plant in operational condition. Therefore increasing the capacity of the plant based on slurry route is not possible even introducing pipe reactor.

Next remarkable problem at the plant is preneutralization tank for reacting phosphoric acid and sulphuric acid with ammonia together with addition of scrubber's liquor consisting of the following:

- 1) Difficulty in pumping and metering the hot slurry from the preneutralizer.
- 2) Foaming and boiling over of the slurry in the preneutralizer.
- 3) Difficult in controlling the slurry level in the preneutralizer
- 4) Plugging of the ammonia sparger and poor ammonia distribution in the preneutralizer.
- 5) Scarcity of drying the product

By this proposal for increasing the capacity of existing DAP/NPK plant neutralizer will be avoided.

Production of NPK grade 15-15-15 cause lot of problems because of crystalline structure of ammonium sulphate (AS) and the production capacity is 1000 MTD only. This grade 15-15-15 could replace 19-19-19 for purpose of start using of fertilizers and thus minimizing the need for granular urea for 19-19-19. Therefore it is better to keep 15-15-15 in production program but is necessary to improve operational conditions and increase capacity to minimum 1300 MT/D. This is possible by introducing part of ammonium phosphates in the form of MAP powder. It will also keep the production of ammonium sulphate even is falling the interest of using it as fertilizer.

B. TECHNICAL FEASIBILITY FOR CAPACITY EXPANSION OF EXISTING DAP/NPK PLANT

The need for increasing the capacity of DAP/NPK plant is in the requirements of the Project Master Plan to reprocess 800 MT/D P₂O₅ of phosphoric acid what is not possible by producing DAP on both plants only, as already recognised. To solve this problem it is possible either by lower the quantity of phosphoric acid production and import the rest of DAP required or to increase the capacity of existing DAP/NPK plant and adjust capacity for the new DAP/NPK plant accordingly. Here after is considering possibility of increasing the capacity of existing DAP/NPK plant and to choose the technology for the new DAP/NPK plant.

Possibility of using big recycle ratio 4:1 built in the unit for changing mode of operation by producing grades required lower recycle ratio could be the base for increasing capacity of existing DAP/NPK plant and will be the base to choose the technology for new MAP/DAP/NPK plant.

Having production based on ammonium phosphates, change in the production should go from DAP (P₂O₅.4NH₃) to production of MAP (P₂O₅.2NH₃) based fertilizers or to the mixture of this two (see molar ratio N/P comparison).

Molar ratio N/P comparison

	N/P	CASE
MAP 12-52	1,17	1
6,43-27,84-27,84 CP	1,17	1
8-36-18 CP	1,17	1
8-34-17 SP	1,17	1
5-20-30 SP	1,26	1
8-26-26 CP	1,56	2
11,5-34-17 CP	1,71	2
DAP 18-46	1,98	3
10-26-26 CP	1,95	3
12-30-15 SP	1,98	3

From the molar ratio N/P comparison could be seen the differences between 3 cases. Ammoniation of phosphoric acid is achieved by producing monoammonium phosphate (MAP) at first. By further ammoniation will be increased molar ratio between N and P₂O₅ coming closer to the diammonium phosphate (DAP).

DAP is unstable above 80 oC and is losing part of ammonia when drying DAP or NPK based on DAP. Together with losses throw ammoniation total losses are about 10%. To

void losses on ammonia is recommended to stop ammoniation process between production of MAP and DAP as suggested in the CASE 2. Advantages for CASE 2 are as given for solids route production in comparison to disadvantages for BASE CASE.

There is also important influence on ratio between NH_3 and P_2O_5 if producing DAP or DAP based NPK on phosphoric acid produced from Riecito rock. Because of high content of R_2O_3 ($\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$) in Riecito rock ratio between R_2O_3 and P_2O_5 is above 0,1. Therefore will be not enough phosphoric acid water soluble to react with ammonia to produce high grade DAP 18-46, which will be lower in nitrogen. Thus even BASE CASE will require more granular urea as planned now. Anyway will be necessary to agree the slightly lower NPK grades for marketing than foreseen now because of sludge in phosphoric acid. Quantity of sludge will differ according to the time available for settling in storage tanks before used in DAP/NPK plant. To have always the same quality in fertilizers when marketing will be necessary to compensate the differences in the quality of raw materials by addition of filler in DAP/NPK plant.

First proposed base grades for production on MAP/DAP/NPK plants for Moron are below N/P ratio 1,4 (CASE 1) thus the losses on ammonia are small and easily recuperated by scrubbing system. Base grades could be improved to the mol ratio 1,7 (CASE 2) as shown above and still losses on ammonia could be recuperated. But going up to the mol ratio of 1,98 (CASE 3) losses on ammonia will be 10% or more even with good designed scrubbing system.

To be able to increase the capacity of existing DAP/NPK on above change of mode of operation it is necessary to have the possibility of using MAP powder in granulator to operate on "solids route" base and make a fundamental difference in the mechanism of granulation by the "solids route" and "slurry route" respectively. In the case of the solids route, the system is "granulation efficiency controlled". The procedure is to establish the optimum pH and granulate with steam to achieve the maximum possible generation of product size material in the granulator. Instead of steam, liquid phase necessary for good granulation could be introduced in the granulator as: phosphoric acid with lower concentration such as 40% P_2O_5 after using in scrubber, then also in granulator down to 30% P_2O_5 for the reaction with ammonia, then slurry directly from MAP reactor and slurry from pipe reactor or pipe cross reactor. Relation between solids phase and liquid phase is 30-70% of solids depending of the grade produced and capacity required.

This results after screening in the minimum amount of fines and oversize being recycled to the granulator.

Simplicity of operation is the main advantage of solids route and is basis for all the other advantages. Once established process parameters needs very little control with next advantages also:

- No significant losses in nitrogen as it is the case when producing DAP or DAP based NPK grades, what is possible to produce also.
- Process potash salts in powder form and it is no need to import granular form for Magfer and even is possible to produce higher grade in potash such as 7-20-30 to suit requirements for potash for remained 20% of grades mixed in small quantities.
- Producing at high capacity granular MAP per time would help in keeping level in acid storage tanks constante.
- Increasing capacity of the existing DAP/NPK plant up to 1500 t/day and even more for some grades.
- No segregation during transport and application of Bulk Blender's (MAGFER) product.

For production of MAP powder it is necessary to built adjacent to the new DAP/NPK plant facilities to produce MAP powder which main equipment consist of:

MAP reactor

The reactor operates under slight pressure (2 bars) thereby enabling a true solution to be formed. The largest one built up to date has diameter of 3,8 m and is fabricated in Incoloy 825 material because of corrosion implications by using different phosphate rock.

MAP spray tower

MAP solution from reactor can be sent either directly to the granulator, as feed for slurry route grades, or to the spray tower for direct production of MAP powder. MAP powder in the form of micropills can be used directly as a fertilizer but more commonly it is considered as an intermediate which can be conveniently granulated in low recycle plants either on site or in other locations. The spray tower itself is of a relatively cheap construction being essentially a plastic curtain strapped loosely to conventional structural steel work. In connection with above reactor this is the largest MAP tower designed to date with a single spray nozzle having capacity of 1200 MT/D.

SCRAPER

In the bottom of the MAP spray tower is positioned scraper of very simple design having function to collect micropills on to belt conveyer.

Pipe cross reactor (part of granulator-removable)

As further feature, a pipe cross reactor could be used for certain grades where its use could result in operational cost savings. For instance solids route give higher capacity for about 20-30% comparing with slurry route, but adding pipe cross reactor to solids route gives even higher capacity. Especially it is interesting when producing granular MAP throw solid route and by addition of pipe cross reactor could get grade 11-55 with polyphosphate content of 10-17 per cent, what is beneficial for Riecito rock.

The pipe cross reactor is 150 mm in diameter and should be manufactured in Hastelloy C-276.

MAP scrubber

For washing the gases from MAP reactor it was installed only one scrubber by now as shown on the flowsheet because of the strict pollution regulation. For Moron is expected that will be no necessary.

C. MODIFICATIONS ON EXISTING DAP/NPK PLANT

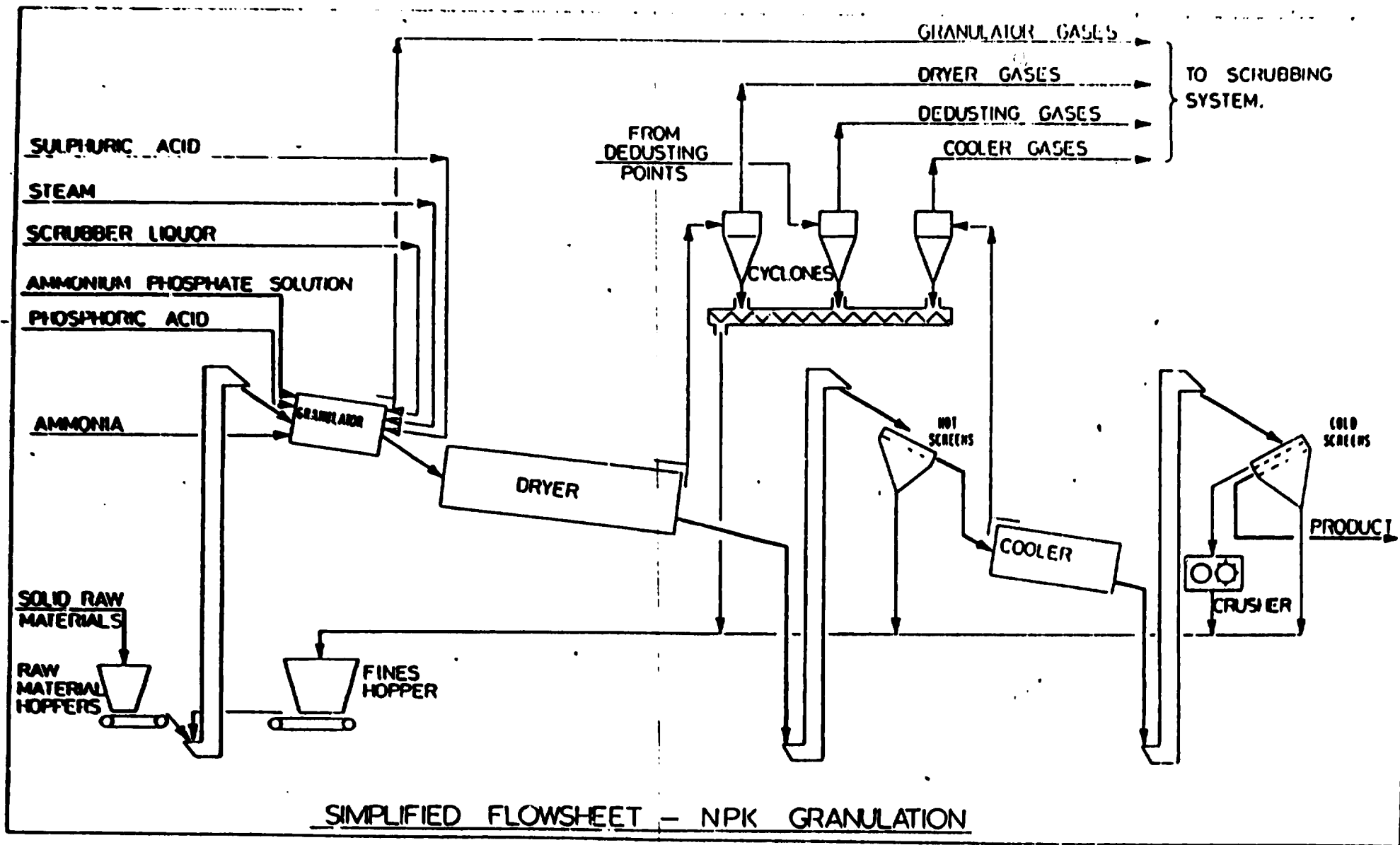
For increasing the capacity on existing DAP/NPK plant would be necessary some checking and minor modification such as:

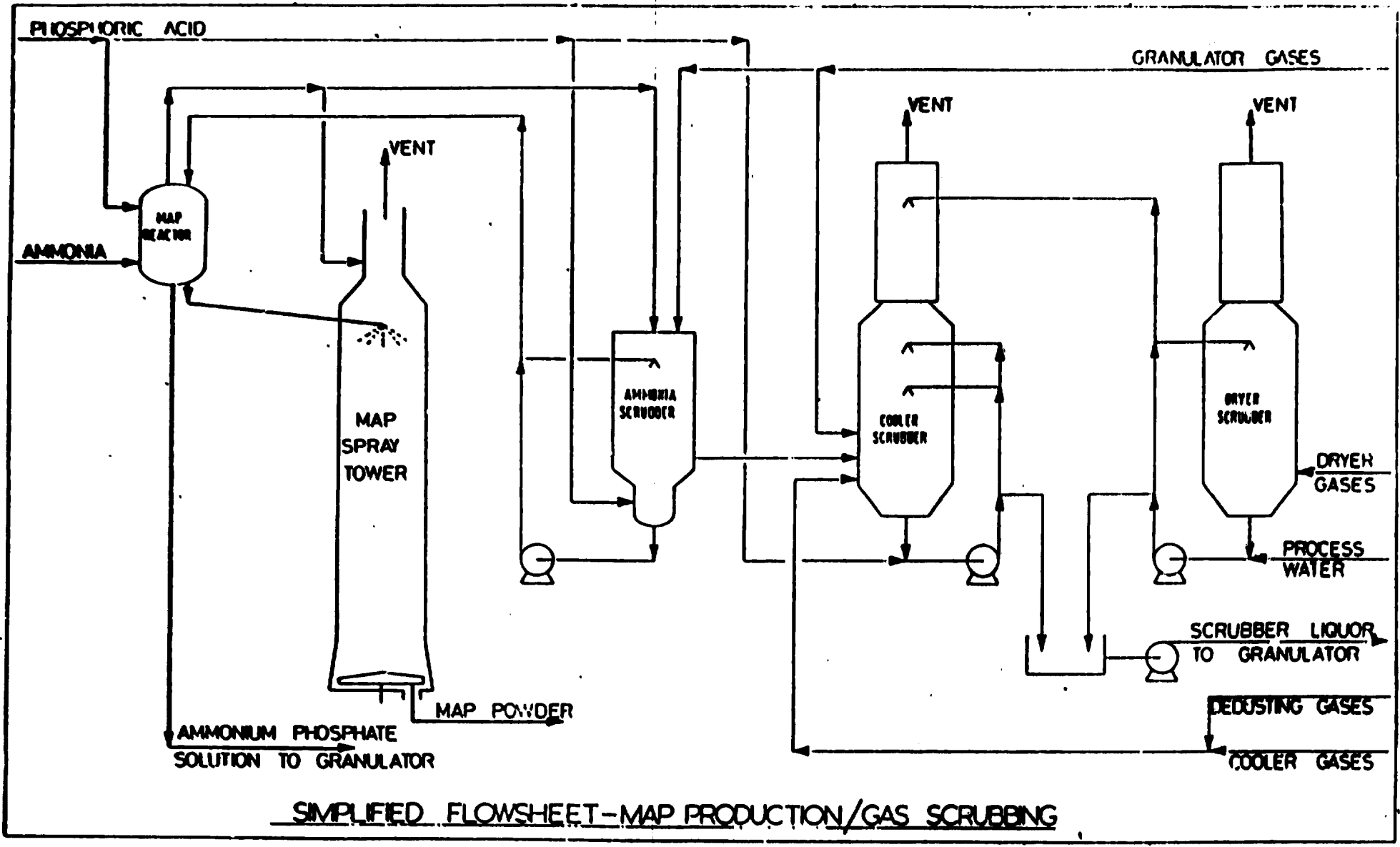
- Checking capacity of raw materials metering equipment to suit quantities of MAP powder required (35 MT/h based on 8-26-26 and 10-30-20).
- Connection from scrubber system to granulator to introduce directly scrubber liquor in granulator.
- Connect phosphoric acid and sulphuric acid lines to granulator.
- Rearrange sparger in granulator to accept above raw materials and removable pipe cross reactor

Production process for producing DAP and NPK grades will be based on solid MAP powder and liquid phase which will consist of:

- pipe cross reactor slurry
- phosphoric acid 30%, 40% and 50%
- sulphuric acid
- ammonia
- scrubber liquor
- steam

For liquid phase will be used all as previously mentioned except slurry from MAP reactor which will be used on new DAP/NPK plant because it is not known now if new DAP/NPK will be positioned close enough that MAP reactor could serve both plants with slurry.





D. TABLES (enclosure 1)

For explanation of additional tables it is necessary to add following:

- Case 1 is based on production of NPK grades suitable for blending with urea at Magfer units. NPK grades produced at two MAP/DAP/NPK plants are based on the mol ratio $N/P \leq 1,2$ and require more urea granular for blending than other two cases. For case 1 and production program for 1991 year will be necessary 52.000 MT/Y of granular urea. This will require increase in the capacity of production of granular urea from 248.000 MT/Y to 300.000 MT/Y about 20%. Advantages for this case 1 are already given for solids route and apply to the case 2 also.
- Case 2 is based on production on NPK based grades with mol ratio $N/P \leq 1,7$ and are suitable for blending with urea or for direct application as start fertilizers. Quantity of granular urea required according to production program for 1991 year are 22.000 MT/Y what require increase in the capacity for production of granular urea from 248.000 MT/Y to 262.000 MT/Y about 10% and maybe is not necessary to increase the capacity for production of granular urea.
- Case 3 is the same in principle as BASE CASE, but instead of producing DAP will be produced NPK grades based on mol ratio $\leq 1,98$ that is DAP based NPK grades. Disadvantages according to the CASES 1 and 2 are in lower capacities and up to 10% losses on ammonia. Required quantity for granular urea are naturally the same as foreseen in BASE CASE.
- MAGFER units should be dimensioned at the place where they belong and that is distribution system (Palmaven) on the next basis:
 - A. Quantities of fertilizers for first application higher on nitrogen
 - B. Number of grades required in small quantities
 - C. To produce grades they can do easier than DAP/NPK plant
- Investment cost for phosphoric acid and MAP/DAP/NPK plants are given for comparison purpose only but capacities are as required.
- Number of grades for each CASE correspond to the

number of required grades as finished product. It means that will be chosen just one CASE as a base for production program of NPK grades for 5 finished grades or 5 base grades from 3 CASES. Thus distribution of all NPK grades plus MAP and DAP on two MAP/DAP/NPK plants will results in less grades for production per plant than now in one DAP/NPK plant.

- Normatives are given for the base production of NPK and for the total consumption of finished product together with the summary.

- For calculation of required working days for production of NPK grades on both MAP/DAP/NPK plants have been used capacities from CASE 3 to be on the save side and that is for NPK = 1300 MT/D and for DAP = 800 MT/D.

CASE 3:

NPK	573.016:	1300 =	440 days
DAP	146.000:	800 =	182 days
	TOTAL		622 days

CASE 2:

NPK	514.775:	1300 =	396 days
DAP	146.000:	800 =	182 days
	TOTAL		578 days

CASE 1:

NPK	484.231:	1300 =	372 days
DAP	146.000:	800 =	182 days
	TOTAL		554 days

As above only CASE 3 require more than 300 working days per year per plant.

Proposed licensors to suit above requirements are:

- Norsk Hydro, U.K.
- Rhone Poulenc, France

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Based on Project Master Plan and this report it is possible for Corporative Planning Division to prepare final document for Project Team on which basis they could further work on this project. Next improvement on this project is possible to do only by approaching the licensors. It is not necessary to approach licensors through some independent institution because Pequiven's engineers could do it directly.

Rehabilitation of existing phosphoric acid plant and the way how to choose the process for new plant should be considered together from the process point of view up to the offsite facilities as explained in the report. Experience gained by design for rehabilitation of existing phosphoric acid plant should be used for design of new phosphoric acid plant whenever applicable.

Expansion of existing NPK/DAP plant is necessary to suit the P2O5 balance foreseen in Master Plan. On the basis of this expansion should be chosen process for the new NPK/DAP plant. Flexibility in operation of both NPK/DAP plants will help not only to suit planning requirements but will be applicable to any different requirements coming in the future as a result of developing the application of fertilizers in Venezuela.

For realization is suggested CASE 2 which is very close to BASE CASE in requirements for granular urea, but has a lot of advantages as explained. It should not be considered CASE 2 as a change in conception from BASE CASE because final results at MAGFER units are the same and gives possibility for direct use of NPK. More applicable to CASE 2 is definition that CASE 2 represents improvement of previous experience in easier production of NPK versus production of DAP.

It will be necessary to import next quantity of solids raw materials:

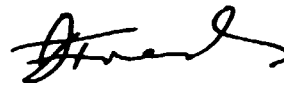
- 100.000 MT/Y sulphur
- 180.000 MT/Y potash salts
- 300.000 MT/Y raw phosphate

Enclosure:

1. **Tables**
2. **Updating Process Technologies for production of phosphoric acid**
3. **PEC processes**

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