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Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

ASSIMILATION AND DEVELOPMENT OF IMPORTED PHOSPHATE FERTILIZER TECHNOLOGY

Wang Jiangping and He Haoming
Guizhou Hongfu, China

ABSTRACT

This article introduces the imported technologies by China Wengfu (300×103 t/a phosphoric acid and 2×400×103 t/a GTSP) plants, and its process of assimilation and innovation of the technologies. Through innovation, the capacity of the imported PA plant has been increased to 400,000 t/a , and GTSP plant was transformed into a 2×600,000 t/a DAP plants to meet market demand. From the recovered DAP waste gases, the first in the world, a DAP-MAP combining process was developed, that can benefit from the reduction of the production cost, and improving the competitive level of Chinese ammonia phosphate industry.

1. INTRODUCTION

China Hongfu Industrial & Commercial Development Co. Ltd is a state-owned company, which is engaged in phosphate mining and fertilizer processing, with its main bodies of Wengfu Mine and Wengfu phosphates established in the 1990s and financed by the World Bank and Japanese OECF respectively. The equipments and processes imported from overseas are relatively modern at international level. They have reached the following capacities: 3.5million t/a of phosphate mining, 2.5million t/a of beneficiation, 700,000 t/a of phosphoric acid, 1.68million t/a of DAP/MAP production, 13,000 t/a of yellow phosphorous, and 70,000 t/a of other industrial phosphate and animal feed ingredients. The revenue in 2003 reached USD 220 million, of which the oversea revenue was about USD 120 million.

Wengfu Phosphates' construction started in 1996 and operation started in 1999, originally included a 2×400,000 t/a sulfuric acid plant with pyrite, a 300,000 t/a phosphoric acid plant, a 14,000 aluminium fluoride plant and a 2×400,000 t/a GTSP plant. Since 2001, through some capacity potentiality exploiting and innovation, the above plants were expanded to the following capacities: sulfuric acid 1.4million t/a, P2O5 700,000 t/a, DAP 1.2million t/a, and MAP 480,000 t/a.

Wengfu's ammonia and phosphate are produced on basis of international standards, and its quality control system has passed ISO 9002 evaluation. Now the Hongfu DAP has become more and more popular in China, and was honored with "Chinese famous brand" in 2003.

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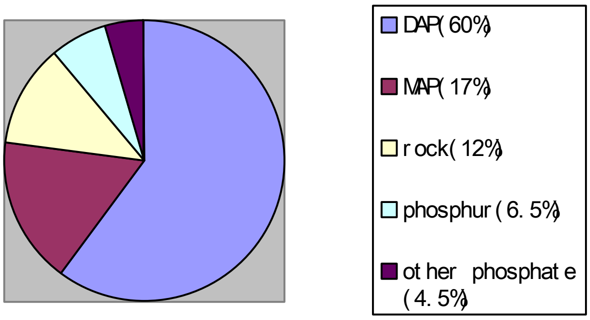
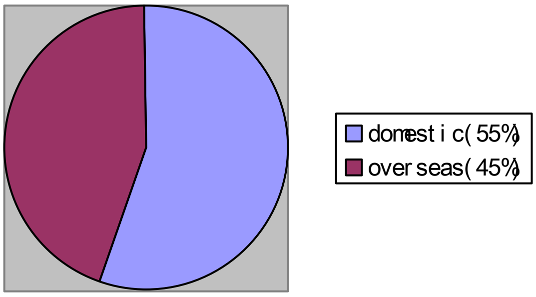
E-mail: worange@21cn.com

The followings are the Hongfu products mix and their market structure.



Dia.1 China Hongfu products mix



Dia.2 China Hongfu markets structure

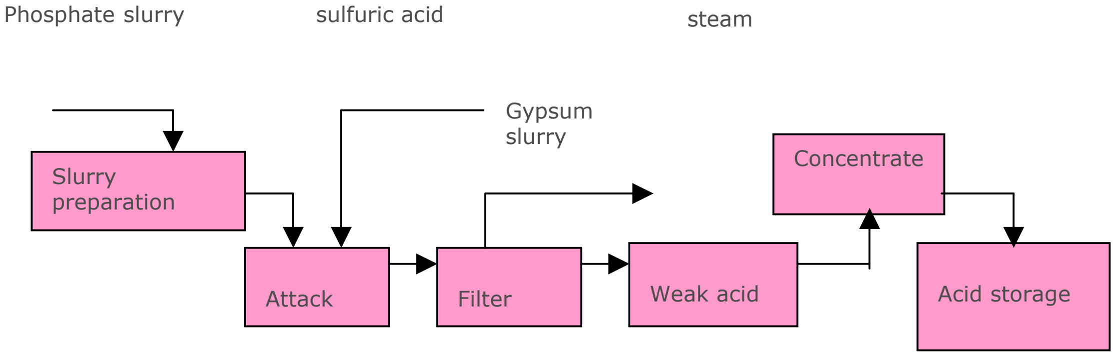
2. ASSIMILATION AND DEVELOPMENT OF THE PHOSPHORIC ACID PRODUCTION TECHNOLOGY

2.1 The Imported Phosphoric Acid Technology

Wengfu's imported phosphoric acid plant consists of the following sections: phosphate slurry preparation, attack and filtration, gypsum transportation and storage, acid concentrating.

The process description as follows:

Dia.3 The process diagram for Wengfu P_2O_5 plant



- Phosphate Slurry Preparation

The phosphate slurry with solid content 60% is transported from the beneficiation plant into the thickeners of this section. After thickening to 70% solid content, the slurry will be pumped to the storage tanks for preparation.

- Attack and filtration

Before going into the attack tanks, the sulfuric acid 98% will be mixed with the recycle acid in a T-type mixer, and then react with phosphate slurry in the attack tank. The amounts of the acid and phosphate are controlled by a ration adjusting system, and normally by adjusting the acid amount to keep the necessary conditions. The reaction of sulfuric acid and phosphate produces a large amount of heat, which, together with the additional dilution heat of sulfuric acid, leads to rapid increase of the temperature of reaction slurry. In order to keep the temperature condition for the dehydrate forming of phosphate gypsum, a vacuum cooler is used for cooling the reaction slurry. Through the digestion of the reacting slurry, the gypsum critical size grows, and then the slurry is pumped to the filter to separate the weak phosphoric acid(28%P2O5) and gypsum.

- Acid concentration

After thickening, the weak phosphoric acid from filtration is sent to this section for further concentrating in order to be as raw material for downstream plant. The under stream from the weak acid tank(s) is recycled to the attack tank(s). In the concentration section, the forced recycling single stage heating and vacuum vaporization process is hired by 0.5mpa steam. The output product from the concentration is 50-52%P2O5 acid which will be stored in the final acid tank(s).

- Gypsum transportation and storage

One ton of phosphoric acid production yields 4.8 tons of gypsum, which is discharged in slurry pipeline and the contained water is then recycled from the gypsum tailing dam for reuse .

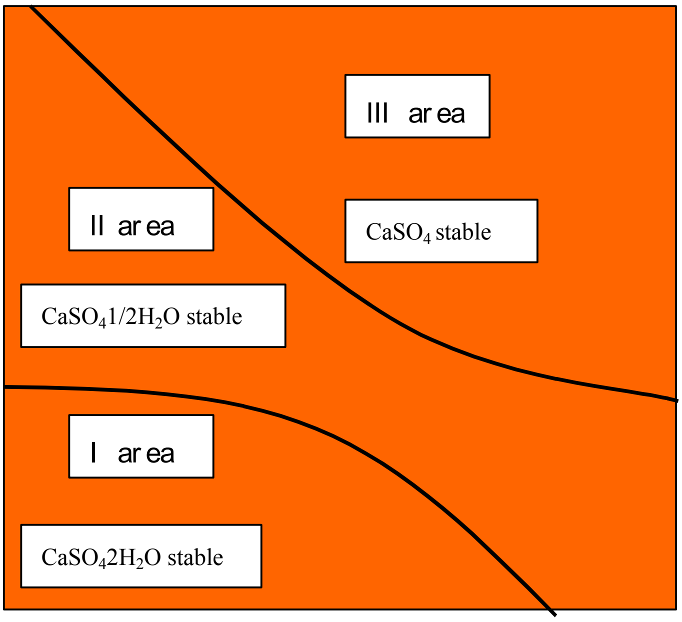
2.2 Study and Practice on Enlarging the Capacity of the Phosphoric Acid Plant

2.2.1 Theoretical Basis

The chemical reaction between phosphate attack and sulfuric acid can be described as follows:

$Ca_5F(PO_4)_3+5H_2SO_4\ nH_2O = 3H_3PO_4+5CaSO_4nH_2O +HF$

There are 3 kinds of calcium sulfate crystals in phosphoric acid solution: CaSO4? CaSO41/2H2O and CaSO42H2O. Some people studied the transfer condition of the above crystals, and made the CaSO4-H3PO4-H2O 3-phase diagram(Figure4).In figure.4, Area I is a stable area for dihydrate, but the operation temperature there must be kept under 40oC. Therefore, a big amount of heat must be removed to realize the temperature condition in industrial plant. Additionally, the slurry in this temperature is too viscous to be pumped and filtered, so phosphoric acid production is not normally operated in this area. On the contrary, in Area III, the temperature is too high, and the corrosiveness of the reaction slurry is comparatively too strong, consequently demanding much higher of the construction materials, and therefore affecting the plant operation efficiency. Even though, some plants in the world still operate in the area. In Area II, the dihydrate is stable, taking both advantages of I and III areas, so most phosphoric acid plants are operated in the area.



Dia.4 $CaSO_4$-H_3PO_4-H_2O 3-system phase diagram

The phosphate attack with sulfuric acid includes two transfer processes: firstly, the transfer from the fluoride and phosphate rock to gypsum, secondly, the transfer from the non-stable gypsum to stable gypsum. The first transfer happens before the second, and faster than the second, so we think the second transfer, gypsum transfer is the key item needing to be considered in the phosphate attack. The gypsum transfer dynamics was studied by some scholars, and the result is : This transfer can be separated into two stages. One is the transfer preparation stage, the other is the actual transfer stage. The total gypsum transfer time consists of the two stage time. As shown in Figure 4, in the dehydrate process, the hemihydrates are produced first and then, the transfer from hemi-hydrate to di-hydrate happens, and the time of the transfer determines the capacity of a plant. There are many factors affecting the above gypsum transfer, but the SO42- is the critical one in addition to the temperature and PO43-. As to the transfer process from CaSO41/2H2O to CaSO42H2O, the logarithm of transfer time is the linear function of the temperature or phosphoric acid concentration, with a positive variable coefficient, indicating that the higher is the temperature or phosphoric acid concentration, the longer the transfer time is [1].

The affecting extent from SO42- on the transfer has something to do with the phosphate rock category. And there exists an optimal condition to reach the highest transfer rate. The optimal condition depends on the experimental analysis of the phosphate rock employed.

Based on the above analysis, in order to enlarge the capacity of the existing 1000tpd P2O5 plant, the following items have to be studied firstly:

- After enlarging the capacity, the reaction slurry temperature will increase, then we need to ask: does the final temperature still remain in the stable area for dehydrate? And can the constructing materials of the plant and equipments endure the new condition? If not, we need to reconsider the capacity of the cooling system.
- Is the slurry residual time in the attacking and digestion sections long enough to allow the gypsum transfer and crystal growth, which then to facilitate the later filtration and washing?

Through some necessary studies and calculations , the following results reached:

(1) If the capacity of Wengfu Phosphoric Acid plant is enlarged by 30%, the reaction slurry temperature will be increased to 80-82oC,but enlarged by 50% capacity enlarging, the temperature will be 82-85°C. This means the system is still in the condition of the di-hydrate reaction area, but it is close to the temperature upper limit of the equipments materials. So if additional cooling capacity is available, it will improve the system's operation.

(2) The residual time of the attacking and digestion section for Wengfu's case is 4.8 hours, and will be 3.25 hours with a capacity of 130%, which is still long enough for the reaction and gypsum transfer.

(3) After the enlargement, the gypsum washing rate is possibly lower than before because of the lower residual time, possibly leading to some phosphorous loss. The allowable economic P2O5 recovery rate is about 91.18% according to the cost of Wengfu's phosphate rock mining and processing.

2.2.2 Study and Experiment for the Capacity Enlargement

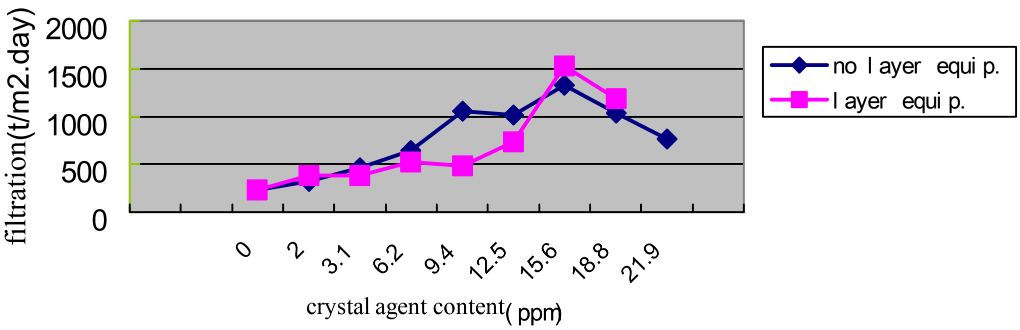
The above studies are from the basis for the enlargement. Additional studies need to be performed such as checking the specifications of each equipment, improving the reaction and filtration conditions, etc. [2]

(1) Checking the Specifications of Key Equipments and Piping Items

Based on the balance studies from the mass, heat and water in the attacking and filtration systems, we checked not only on the specifications of each key equipments and piping, and also the running conditions of the equipments with 100-110% capacity. The results from the studies are as the follows: the capacity of the most pumps and piping are enough for 130% enlargement, but the running life time of most components can be decreased because of the corrosion and erosion. The additional methods, such as modifying the way for mixing and feeding of phosphate and sulfuric acid, and adding the crystal agent, etc., can be used for improving the system conditions. On the capacity of 150%, most equipments and piping must be changed due to capability limitation.

(2) Experiment on Improving Gypsum Filtration by adding Crystal Agent

In order to make the gypsum crystals grow rapidly and to increase the filtration capacity, the experiments, aiming at improving gypsum filtration with the addition of a crystal agent, were conducted with the following results: crystal agent can obviously improve the gypsum filtration condition, and there exists an optimal agent content range in which the gypsum filtration is the best, especially after the reacting slurry under gone through the layer separation facility, result is much better(Figure 5).



(3) Project Modification

On the basis of the above studies, we arrange the following modifications to the existing plant:

- Modification to the mixing of phosphate, sulfuric acid and recycled acid
- Crystal agent and layer separation system
- Underflow recycle system for the weak acid storage tank(s)

2.2.3 Enlargement Practice and Results

Since the innovation was completed, the plant operates at 130% of the original design capacity, and went through commissioning of more than 2100 hours. In Aug. 2002, we conducted a 72 hours performance test, the followings are the test results:

- Capacity:1308 tpd P2O5
- Average phosphate recovery rate:95.07%
- Main raw materials consumption: rock 3.08t/t p2o5, sulfuric acid 2.63 t/t p2o5 (excluded the recovered weak sulfuric acid from the sulfuric acid plants)
- Main process indicators:
    - Slurry temperature in the attack tank(s): 79-81oc
    - Density of the filtration slurry: 1.29-1.32g/ml
    - Free SO3: 25-35g/l
    - Solid content of the attacking slurry: 25-37%

2.3 Significance Phosphoric Acid Enlargement Performance

The successful enlargement is a good model of Hongfu "decreasing incremental input" program. With a much comparatively less additional investment in this enlargement innovation, we harvest a lot, i.e., additional 100,000t/a P2O5, facilitating the material balance for the downstream plants.

Through this enlargement innovation, the technologies of fast attack, gypsum crystal improvement and crystal layering were firstly put into use in a big phosphoric acid plant successfully. And besides, the innovation process serves as a rewarding exploration on applying the domestically-made engineering materials in phosphoric acid production application. We are sure that the above practice experiences will be helpful for China to develop large-scale phosphoric acid plant technology of its own.

3.TECHNOLOGY AND PRACTICE FOR THE CONVERSION OF GTSP TO DAP PLANT

3.1 Imported GTSP Technology

3.1.1 Process Description

Wengfu GTSP plant includes two fully identical production lines, each with the capacity of 400,000t/a, with the process as follow:

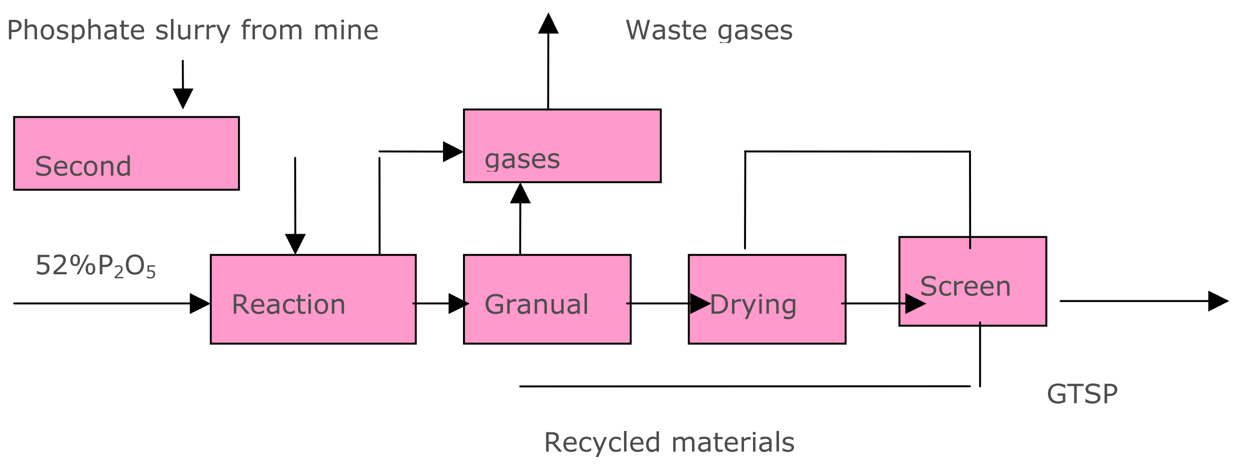


Figure 6: Process diagram of Wengfu GTSP plant

The solid content 68% phosphate slurry coming from Wengfu mine, of which 60% passing minus 200mesh(i.e.60%-200), will be ground for a second time to be the solid content 65% slurry with size of 80%-200. Together with the 52%(P2O5)phosphoric acid , the phosphate slurry will be pumped into the reactor to form the TSP slurry which is then pumped into the granulator, where the granules are shaped and coated together with the recycled TSP materials. The coated GTSP will be delivered to and dried in the dryer before being screened in the two-stage screening system.

Those output that satisfy the size requirement are sent to the bagging system as qualified GTSP product, and the remaining output are recycled to the granulator.

The waste gases, discharged from the reactor/granulator/dryer/cooling and de-dusting system, will be scrubbed in the respective washing towers before being released into the atmosphere through a stack. The washing water will be recycled repeatedly until reaching certain concentration and then be pumped to the waste water treatment station.

3.1.2 GTSP Market

When Wengfu GTSP started up, it was during the TSP market recession period. During the years between 1998 and 2002, the total consumption of TSP in China was less than 200,000t,and the operating of Chinese TSP plants was lower than 15%. On the other hand, the situation for DAP in China was quite different, with DAP demand remaining at about 5million tones each year, with the domestic supply was lower than 50%. Based on the fact and the future market forecast, in June of 1999, we started to build the ammonia supply station, and decided to convert the GTSP plant to a DAP plant.

3.2 The Engineering Study and Practice on the Conversion from GTSP to DAP

In order to market new product, and keep the upstream plants running, the conversion project was divided into two steps:

- First step: "emergency conversion", which means to take the following process: pre-neutralization + granulating + gases scrubbing with sulfuric acid.
- Second step: "permanent conversion", which means to take the process of: pre-neutralization + pipe reactor + gases venturi scrubbing with phosphoric acid and sulfuric acid

The "emergency conversion" requires smaller investment and shorter time because it keeps on employing GTSP scrubbing system, but the process consumes too much raw materials, especially ammonia. By contrast, the "permanent conversion" process makes great changes to the gas scrubbing system and need to improve the GTSP de-dusting and screening facilities a lot, which demand much more investment as well as more time but give rise to much greater returns by substantially promoting the plant running rate, capacity, product quality, and by reducing the raw material consumption rate. Table 1 shows the operation data for Wengfu DAP plant since 2000, indicating the basic success:

Table 1 Operation data for Wengfu DAP plant

year	Output (t)	P_2O_5consumption (t/t)	NH_3consumption (t/t)
2000	107,000	0.510	0.270
2001	318,000	0.500	0.240
2002	502,000	0.490	0.232
2003	700,000	0.488	0.225

3.2.1 The Key Points for the Conversion from GTSP to DAP

(1) DAP Process Description

Together with gas ammonia in a certain proportion, 48%(P2O5)phosphoric acid is pumped into the reactor to form DAP/MAP slurry, of which the mol ratio of NH3/H3PO4 is 1.4. The slurry is then pumped to the granulator, where the recycled DAP materials are coated and ammoniated for the second time, and then the coated DAP will be dried in the dryer, and screened in the recycle system, and cooled and dust-removed. And then the qualified DAP product can be sent to bagging system, with the unqualified being recycled to the granulator.

The waste gases, from the reactor/granulator/dryer/cooling and de-dusting system, will be scrubbed in the respective washing towers, and then to the atmosphere through a stack. The washing slurry will be recycled repeatedly until reaching certain concentration and then pumped back to reactor for recovery, and at the same time, the fresh phosphoric acid and sulfuric acid are added into the scrubbing system.

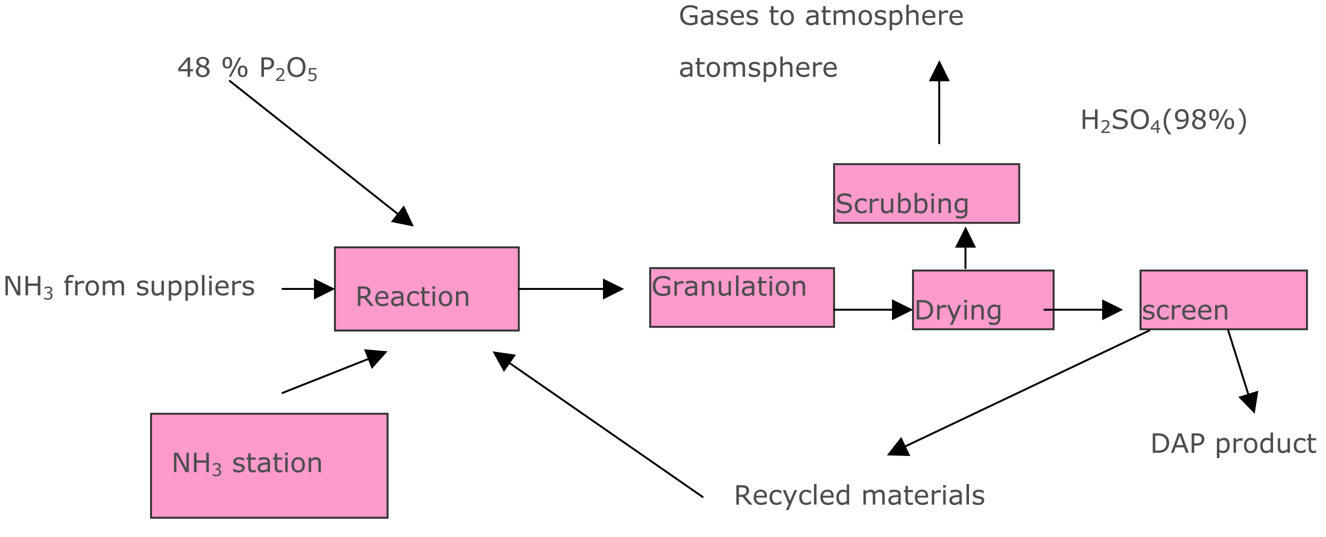


Figure 7 Process Diagram for Wengfu DAP Plant

(2) Key Modification Items of the Conversion

As the above description, there are two steps to convert Wengfu GTSP to DAP. The followings are the key items involved in the what we called "permanent conversion" process:

- Ammonia supply station

The supply capacity of the station is 200,000t/y NH3, including containers, downloading facilities, etc.

- Reaction and granulating system

For DAP production, the ammonia supplying piping system is needed in the reactors and granulator, and so are the recycled slurry pipes to recycle the washing liquid back to the reacting system. The driving system of granulator needs to be modified to run in two directions in order to let the materials discharged at the other side of the ammonia nozzles while the granulator is shut down.

- Recycled materials system

In Wengfu's case, the original conveying capacity for GTSP has about 25% of surplus when it works for DAP production, so it is unnecessary to modify it. But the temperature going through the dryer needs to be decreased, because the GTSP can be dried in 450-550oC while for DAP the temperature should generally be kept under 300oC,otherwise, DAP will be melt or decompounded, causing ammonia loss.

- Scrubbing system

For DAP production, there are some kind of ammonia and dust to be discharging from the reactor, granulator, dryer and other equipments. In order to recover them, some modifications should be considered :firstly, adding some phosphoric and sulfuric acid into the washing liquid , and recovering the liquid for reuse. Secondly, employing two-stage venturi scrubbers before the existing scrubbing tower, and at same time, replacing the waste gas fan with a more powerful one to keep the minus pressure in the waste gas scrubbing system.

3.2.2 The Main Problems after the Conversion from GTSP to DAP.

Even though the slurry GTSP process is similar to the DAP process, there are some differences in production control because of their different medium properties. The followings are the main problems after the conversion from GTSP to DAP.

(1) Problem of "Poor Granulating Behavior"

What we called "poor granulating behavior", means that the normal distribution of particle size at the outlet of the DAP granulator cannot be controlled accordingly by adjusting process parameters. At this time, we find that the sizes of the granules go to the two opposite extremes, with the on-specs materials less than 10%, and the sizes between ?100mm~?200mm accounting for over 60%. Even worse, they take the shape of clumps or dumplings, with the inside wet and the outside dry. To bear such bulky materials, the ammonia supplying piping system within the granulator is easily distorted or even broken by the shearing forces therein. It is also likely to jam the discharging channel, leading to the plant shut-down. Additionally, the above case probably causes partial granulated materials over-ammoniated and produces too much dust, which may cause the de-dusting system collapse.

The DAP coating granulation principle was discussed through the study on the characteristic of the solid materials in rotary drum.[3] The conclusion is: it is necessary to use ammonia stream to break the radial segregation center so that the fine particles can be entrained to flow through the slopping layer, and coated by DAP slurry. On a constant ammonia pressure, the angle, between ammonia flow and horizontal line, is so critical as to affect the length of ammonia flow directly. A way to calculate for the angle was discussed theoretically. On the basis of the test result, a proposal was compiled for modifying the granulator internals, which solved the problem of poor granulating behavior successfully.

(2) "Ammonia Phosphate Rain" Problem

After the "permanent conversion" finished, the waste gas from the plant stack must meet the state environment standard, but there is a strange problem what we called the "ammonia phosphate rain". It is a kind of white liquid spot and is like raining when it is on, and is especially serious when the weather is under high humidity(80%) and at low temperature(20oC). We understand that is composed of the cooling liquid of the ammonia, phosphate dust and the steam in the gases.

There are quite different physical and chemical properties between the gases from de-dusting system and those from the reaction and granulation system: the de-dusting gases have low moisture(18-20%), while the reacting and granulating gases have high temperature (70-80oC) and high moisture(82%). The low moisture gas and steam can be recovered for reuse. To solve the problem of the "ammonia phosphate rain", we need to decrease the moisture of the gases from reaction and granulation system to the same moisture extent corresponding to the yearly minimal temperature at the plant site. Alternatively we should decrease the dust content in the gases from de-dusting system. There are many engineering items that need to be studied (see 4.2.2). Nowadays we discharge the above two different sources of gases separately and avoid the "ammonia phosphate rain" temporarily.

3.3 Significance to Perform the Conversion Project

It promotes the products mix, and improves the capability of the company to resist the market risk

It is the leader to convert GTSP plant to DAP plant in China, and obtains valuable engineering experiences on modifying large-scale phosphate fertilizer plant.

We discovered a way to calculate the optimal angle between ammonia ejecting and horizontal line based on the segregation theory, and to modify the internals successfully.

4. TECHNICAL STUDY ON UTILIZATION OF GASES FROM DAP PLANT

4.1 Problem

As shown in the above description, some active substances and thermal energy in low level are not utilized but wasted. Besides, the water balance of the scrubbing system does not have enough operating flexibility, which often causes the washing liquors to spill out of the plant to pollute the nearby rivers when cleaning or temporary shut-down occurs. Based on the above reasons, we started the study on the utilization of the wasted gases, i.e. making the wasted as valuable resources.

4.2 DAP-MAP Combining Process

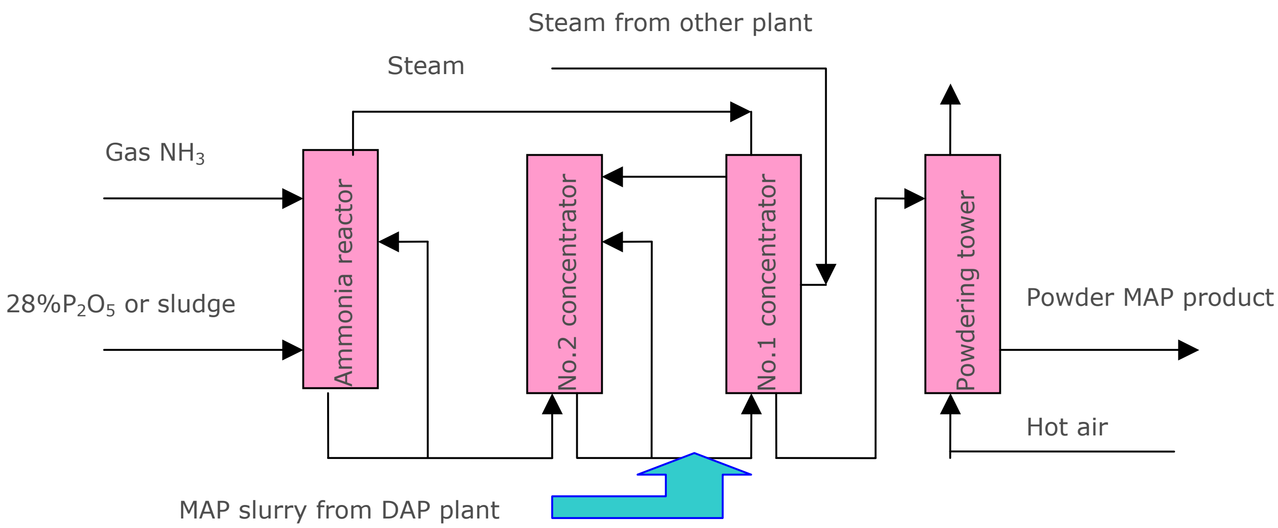
What we here called "the DAP-MAP Combining Process " is an environment friendly process, which makes the MAP slurry by utilizing the active substances and low level thermal energy contained in the waste gases discharged from DAP process, overcomes the thermal-dynamic constraint involved in the waste gases treatment of the DAP producing system and the constraint of the system water balance. In principle, the degree of cleaning of DAP waste gases is the very recovery rate of MAP raw materials. If the project is successful, the "ammonia phosphate rain" problem and scrubbing water balance problem can be resolved. In addition, the ammonia spillage off the reaction and granulation systems will no longer be the constraint for DAP production[4].

The project was divided into two steps as follows:

- Constructing a MAP plant on the basis of slurry concentrating process
- Study to find a proper process and establishment for reaction and concentrating, so as to produce MAP slurry using waste gases from DAP plant.

4.2.1 The MAP Plant on the Basis of Slurry Concentration

As a basis of the project, the MAP plant should be suitable not only for using MAP slurry made from DAP gases but also for using the acid sludge under-flowing from phosphoric acid tank(s), so we built a ammonia reactor with phosphoric acid (28% P2O5) in the MAP plant. The MAP plant has already been put into operation, with capacity of 240,000t/a. The following Figure 8 is the process diagram of the plant.



Dia.8 The process diagram for slurry concentrating MAP

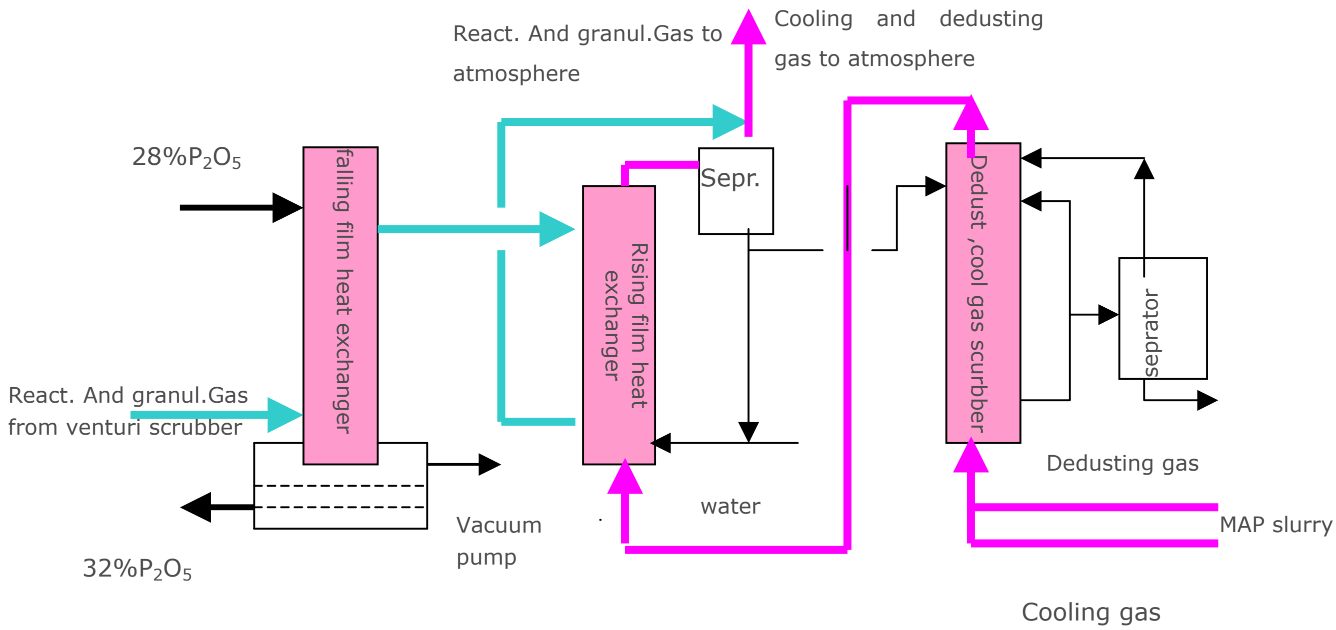
4.2.2 Reaction and Concentration Process taking DAP Gases as Resource

The reaction and concentration processes are critical for the project have two particular characteristics:

Using the low level thermal energy in the reaction and granulation gases from the venturi scrubbers to heat up the 28% phosphoric acid, before concentrating in a vacuum to 32%;

Using the lower moisture de-dusting gases to cool the above processed gases down to 45oC and to decrease the moisture of the reaction and granulation gases, and eventually to put the "ammonia phosphate rain" under control effectively.

The reaction and granulation process is as Dia.9,



Dia.9 The reaction and concentration process taking DAP gases as resources

4.2.3 Innovations in the Project:

Make the combining process of DAP / MAP, first in the world, in which the "slurry concentrating MAP process" is intergraded in the traditional DAP process, and in which the residual substances /waste gases /and thermal energy discharged from DAP plant are fully utilized as the resources for MAP production, and helping to increase usage rates of raw materials and energy significantly. Therefore the innovation improves the ammonia phosphate process by increasing the techno-economic efficiency.

It is the first fully Chinese powder MAP plant with capacity of 240,000t/a, from engineering design, materials of construction, manufacturing to production management.

It is the first to employ the following technologies in ammonia phosphate industry: neutralization checking on line, density checking on line, and the distribution control system(DCS), which stand for a great development of Chinese phosphate processing industry.

5. OUTLOOK

China initiated its phosphate fertilizer industry of the high concentration in late 1980's. Through the development for a bit more than one decade, the total annual production capacity has reached about 5.75million tons of P2O5, of which DAP production capacity is 4.9 million tons and MAP 4.12 million tons. By 2003, the self-supply percentages of DAP and MAP in China have been 62% and 100% respectively. As for Hongfu, the production of DAP and MAP are respectively 0.7 million tons and 0.24 million tons, which account for 21% and 8% of the country's output respectively.

Based on its rich resources, brand advantage, and other competition predominance in the industry, Hongfu devotes itself to the assimilation and innovation of imported technologies, and holds steadfastly the R&D mode of combining "enterprise-college-research institute", and employs the capital expansion strategy with open-minded attitude and seeks for various co-operation with fellow industry members. We are confident that, in the immediate future, a internationalized Wengfu will stand prominently in the phosphate industry of the world.

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