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DEVELOPMENTS IN TSP PRODUCTION:-

SLURRY VERSUS POWDER ROUTE CHINESE EXPERIENCE

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INTRODUCTION

The People's Republic of China currently import several million tonnes P_2O_5 per year in spite of abundant phosphate rock reserves within Yunnan, Guizhou and Hubei provinces. Production of fertilizer P_2O_5 in China is currently about 3.75 m tonnes P_2O_5 per year and is mainly consumed in small (tens of thousands of tonnes per year) SSP and FCMP (Fused Calcium Magnesium Phosphate) plants. In order to expand its fertilizer industry and exploit local phosphate reserves, China is prepared to import technology for large scale finished fertilizer plants particularly TSP technology. For the previous three years, Hydro Agri International (HAI) Licensing has co-operated with the relevant Chinese organisations and tested a number of Chinese phosphates for compatibility with their GTSP processes (both Den type and Slurry type processes). As a result of this co-operation, HAI Licensing recently licensed a world scale GTSP slurry process to P.R. China. It will be the first GTSP slurry process to be constructed in China and will have a capacity of 400,000 tpy GTSP and be located in Yunnan Province at Anning, close to the provincial capital of Kunming. HAI Licensing in co-operation with HiTech Solutions of Lakeland, Florida will provide the process design and Mitsui Engineering & Shipbuilding of Tokyo will be the engineering contractor.

This paper will consider reasons why GTSP is popular in China, look at some characteristics of Chinese phosphates with respect to TSP production by both the Slurry and Den processes and finally present some information concerning the Anning GTSP project.

CHINESE REQUIREMENT FOR GTSP

Generally, in order to produce available P_2O_5 from phosphate rock either phosphoric acid or nitric acid is required; and in order to produce phosphoric acid, sulphur is required and for nitric acid, ammonia. Unfortunately for China, neither sulphur nor ammonia production is located close to phosphate rock sources. For example, much phosphate occurs in Yunnan and Guizhou Province in South-West China. These land-locked provinces are about 1,000 km from the nearest sea port and a similar distance from developed indigenous sulphur (see Figure 1).

China is developing infra-structure, but nevertheless the large separation of phosphate and sulphur resources is inhibiting the development of large scale P_2O_5 fertilizer projects.

In spite of these problems, China is pressing ahead with the development of large scale plants, in particular for GTSP production in Yunnan, Guangdong and Guizhou Provinces - the total capacity of these plants is 1.6 million tpy GTSP. The rationale for choosing GTSP for these projects is because in GTSP production some 25% of the available P_2O_5 is provided directly from phosphate rock and does not require sulphuric acid for solubilisation. Thus relative to DAP, TSP does not require ammonia and requires approximately 25% less sulphuric acid to achieve the same level of available P_2O_5 (see Table 1).

A further reason is to restore the fertilizer nutrient balance. China, a few years ago, rapidly developed its nitrogen resources but tended to neglect phosphate. As a result a relative deficiency of fertilizer P_2O_5 has developed and the Chinese are now seeking to restore the balance.

In the case of the Anning GTSP project in Yunnan Province (see below) the absolute in sulphur saving has been made. The project is based on thermal phosphoric acid. The Chinese rationalise the economics because:-

- The problems of delivering sulphur to the phosphate source.
- There is an excess of cheap hydro power in Yunnan province.

Table 1

Sulphur Consumptions

Sulphur requirement per tonne DAP	0.38
Sulphur requirement per tonne TSP	0.27

SELECTION OF GTSP PROCESS ROUTE

There are two main process routes for the production of TSP. These can be collectively described as Den process and Slurry process. HAI Licensing have offered both technologies for Chinese projects.

The main features of the HAI Den process is the production of a powder TSP intermediate followed by a low recycle rotary drum granulation plant. The process can be designed with wide flexibility such that granular NPK fertilizers can also be produced from the same equipment. The advantages of the Den Route are summarised below:-

- Low capital cost for granulation section because of low process recycle ratio.
- Low operating cost because utility consumptions per tonne of product are minimised.
- The Den equipment can be used alternatively and independently of the granulation plant to produce other superphosphates such as SSP, DSP and PAPR.
- Production flexibility; the powder TSP can be used directly for GTSP production or as a raw material for granular NPK fertilizers.
- Low design recycle ratio for the granulation section resulting in small equipment and easier/low cost maintenance.
- Large capacities in a single line are possible (up to 100 tph).

In general the Den route is favoured where phosphoric acid is imported (normally at 54% P_2O_5) and/or where the client requires superphosphate as an intermediate in NPK production in addition to straight GTSP production.

The main feature of the HAI Slurry process is the reaction of phosphate rock and phosphoric acid to produce a TSP slurry which is pumped to a high recycle rotary drum granulation section.

The main advantages of the Slurry Route are:-

- Fully integrated process in which rock and acid are fed at one end and granular product flows from the other.
- Phosphoric acid can be used directly from the hemihydrate process. Therefore neither an evaporation plant nor steam for evaporation is required.

- Lower phosphoric acid concentration required (42% compared to 50% for the Den process). Thus even with a Dihydrate acid plant considerable steam savings can be made relative to the Den process.

- An intermediate maturing store is not required.

- No intermediate solid handling.

- Plant plot size is small.

- Lower labour costs.

The Slurry Route is most appropriate where production takes place on a fully integrated factory with sulphuric acid and phosphoric acid production at the same site and the client requires only GTSP as product.

Our experience in China indicates that the enquiry document will not specify a particular process route and as a result it might be necessary to offer both Den and Slurry processes so that the client can make his own evaluation. (Provided our rock testing proves the suitability of the phosphate for either route.)

The reasons behind the Chinese thinking results from their previous experience in SSP production. Generally in SSP production they use small scale Den type processes and have suffered from fluorine pollution particularly in maturing stores. For this reason Den processes generally are perceived as environmentally unfriendly and old-fashioned technology. On the other hand many of the largest export-based GTSP plants in the world are based on the Slurry process and this is seen as the modern technology. In spite of capital cost differential in favour of the Den process by about 10%, the Chinese are generally looking for reasons to select the Slurry process.

PHOSPHATE ROCK TESTING FOR GTSP

HAI Licensing and its predecessor in the UK (Fisons Fertilizers Ltd) have been associated with superphosphate production since the start-up of the first commercial plant in the middle 1800's. During that time techniques for laboratory testing of phosphate rock for TSP production have been developed and refined.

The tests are used to evaluate phosphate rock performance in both the Den and Slurry processes. The objectives of the tests are to:-

- Specify the operating conditions for the reaction system.

- Specify various raw material conditions such as rock size range, phosphoric acid concentration and temperature.

- Define phosphoric acid and phosphate rock consumptions to achieve a certain product quality (normally available P_2O_5).

- Predict the final product chemical quality in terms of total, water soluble, available and free acid P_2O_5.

- Investigate granulation and drying characteristics.

These objectives are achieved using mainly laboratory scale tests. However results can be confirmed if necessary in batch scale rotary drum granulation and drying tests.

The techniques have been used to predict the performance of Chinese phosphates in the HAI TSP processes. Some details of the phosphate tested are given in Table 2.

Table 2

Chinese Phosphate Rock Tested for TSP

Source of Phosphate	Name of Phosphate	TSP Project
Yunnan Province	Jian Shan Jinling	Anning Yunfu
Guizhou Province	Yingping	Wengfu
Hubei Province	Dayukou	Dayukou

Details of the chemical analysis of the Chinese phosphates tested are given in Table 3.

The Yunnan phosphate sources occur around the provincial capital of Kunming and are quite well developed with the rock used in SSP and FCMP production. The rock is generally not beneficiated and is characterised by relatively high silica contents and low $CaO:P_2O_5$ ratios.

Table 3

Typical Chemical Analysis

Component % wt/wt	Phosphate			
	Jian Shan	Jinling	Yingping	Dayukou
P_2O_5	31.8	31.2	35.1	33.3
CaO	44.7	43.2	50.3	46.8
SO_3	0.38	<0.3	0.63	0.60
F	2.70	2.85	2.92	2.70
Cl	90 ppm	180 ppm	450 ppm	146 ppm
SiO_2	16.2	15.7	3.85	9.13
Al_2O_3	1.04	0.85	0.33	0.44
Fe_2O_3	1.12	0.96	0.35	0.54
MgO	0.25	0.55	1.06	1.77
Na_2O	0.23	0.34	0.16	0.18
K_2O	0.26	0.07	0.17	0.28
CO_2	2.25	2.38	3.70	4.36

Our testwork indicates that some Yunnan phosphates are similar in reaction characteristics to Florida rock. However there are significant differences from mine to mine in rock reactivity with respect to GTSP production. Thus Jian Shan rock performance compares favourably with Florida whereas Jinling rock does not react very well giving products with low available and high free acid P_2O_5.

The Yingping phosphate is beneficiated by a reverse flotation process and our testwork shows it to be suitable for either the Den or Slurry process. The Dayukou phosphate is of low reactivity with respect to TSP production and suffers a high MgO content and as a result the Den process was selected for this project.

An important feature of all the above Chinese phosphates is the very low (less than 5 ppm) cadmium content.

The relative reactivities of Chinese phosphates with respect to TSP production by the slurry process are shown in Figure 2 and compared with Florida and Morocco phosphates. The reactivity index is derived from the equilibrium free acid content achieved in the TSP reaction system operating under standardised conditions. Generally the higher the index the greater the reactivity of the phosphate. From the results it can be seen that the reactivities of the Jian Shan and Yingping phosphates are similar to Florida and Alkalm whereas the Jinling rock is unreactive and is not recommended for TSP production by the Slurry process for the reasons stated above.

The expected product quality over a range of raw material consumptions are indicated in Figures 3, 4 and 5 for Jian Shan, Jinling and Yingping phosphates respectively. The results are summarised in Table 4 which indicates the acid and rock consumptions for each phosphate required to achieve the normal quality standard of 46% available P_2O_5 in the GTSP product.

Table 4

Raw Material Consumptions and GTSP Product Quality

	Jian Shan	Jinling	Yingping
Acid P_2O_5 Consumption (t P_2O_5 per t GTSP)	0.328	0.345	0.338
Rock P_2O_5 Consumption (t P_2O_5 per t GTSP)	0.152	0.138	0.160
Product Quality			
Total P_2O_5	48.0	48.3	49.8
Available P_2O_5	46.0	46.0	46.0
Water Soluble P_2O_5	45.5	44.3	44.4
Free Acid P_2O_5	4.6	8.3	4.5
Water Content	2.5	2.5	2.5

The consumption of acid and rock P_2O_5 is low in the case of Jian Shan phosphate because thermal acid is used which is uncontaminated and therefore not bringing unwanted diluents to the product. In addition because of the low impurity levels the conversion to available P_2O_5 is relatively high.

The main feature of the performance of the Jinling phosphate (using wet process phosphoric acid) is indicated by the relatively high residual free acid P_2O_5 required to achieve 46% a vailable P_2O_5. This factor is also reflected in the relatively high consumption of phosphoric acid.

The Yingping phosphate performs well using wet process acid.

THE ANNING GTSP PROJECT

HAI Licensing tested the Jian Shan phosphate extensively in conjunction with thermal phosphoric acid for GTSP production in both the Den and Slurry processes. Both processes were equally suited to the phosphate. As a result HAI Licensing Slurry GTSP technology was selected by the client for the Anning project. The factory will be located on a green field site about 50 km west of the Yunnan provincial capital of Kunming. The phosphoric acid will be provided from a Yellow Phosphorus plant which will be located on the same site.

The design capacity of the factory is 400,000 tpy GTSP. The GTSP plant will be designed in a single line with a capacity of 60 tph which makes the plant amongst the largest of its type in the world. The quantity of material in the recycle loop of the granulation and drying section of the process will be 540 tph. With a plant of this size the general arrangement of equipment is of critical importance with regard to ease of operation and maintenance and for this reason HAI Licensing have co-operated with HiTech Solutions of Lakeland, Florida who are responsible for developing the general arrangement of the granulation and drying sections. The main objectives are to:-

- Minimise parasitic conveying equipment.

- Minimise the overall height of the building (which in this case will be in concrete).

- Ensure good access for cleaning and maintenance of equipment.

The simplified flowsheet for the process is given in Figure 6. The main process features are summarised below.

Raw Materials and Reaction Sections

The phosphate rock is delivered to battery limits with 65% in the range 50-10 mm and a water content of 8-10%. An air-swept ring roller mill fitted with an air heater has been selected which will simultaneously grind the rock to 80% less than 75 microns and dry the rock to less 1% free water before feeding to the TSP reaction system. The phosphoric acid is delivered to the reaction system at 54% P_2O_5 concentration. The required water balance is maintained in the reactors by returning neutralised scrubber liquor to the TSP reactors.

The two in-line agitated TSP reactors are of conventional design and constructed from RLMS with a carbon brick lining. TSP slurry is transferred from Reactor 2 to the granulator using variable speed pumps to control the flow. Two completely independent pumps and slurry lines will be installed.

Granulation and Drying

Granulation and drying are based on conventional rotary drum equipment. The design recycle ratio is 8:1 and therefore the material throughput of the granulator and drier will be 540 tph. The drums will be manufactured in China. The drier will be supplied with hot air by a directly firing air heater which will be fuelled by the by-product tail gases from the Yellow Phosphorus plant - the main fuel component being carbon monoxide. The drier is designed to reduce the water content of the GTSP to 2.5%.

The Recycle Loop

The equipment such as screens and pulverisers and design of the recycle loop are critical for ensuring a trouble-free balanced operation and to achieve this the following features have been incorporated.

- The maximum proven capacity of a drag flight conveyor on GTSP duty is 432 t/h. For this reason one of the four coarse screens is fed directly whilst the other three are fed via the drag flight.

- Similarly recycle material from three of the coarse screens is collected in a drag flight whilst the material from the fourth screen discharges directly to the recycle elevator boot.

- Single deck screens are specified so that an intermediate elevator is used to elevate the minus 4 mm material to the product screens. The feed to the product screen is adjusted by means of flaps under the coarse screens so that the load on the product screens is as small as is necessary to achieve production rates. In this way product screening area is minimised. Because of the use of an intermediate elevator the overall height of the plant is minimised to save on capital cost for the building.

- Chain mills have been specified for the oversize crushing duty as relatively large machines are available. Therefore only one crusher per screen is necessary.

GTSP is a sticky material and therefore special features have been incorporated to minimise downtime for cleaning as follows:-

- The oversize mills are located directly above the recycle conveyor with large, straight discharge chutes with no sloping surface for build-up.

- The mills themselves are lined with a specially formulated rubber to minimise build-up.

- Any screen or crusher can be taken out of service at any time for cleaning or maintenance.

- All chutes have been oversized to allow operation to continue even with heavy scaling. The chute from the granulator to the drier receives special attention. This chute is made in 316L stainless steel to reduce build-up and loose rubber panels flexed with air cannons are also employed.

Recycle Control

The drier and recycle elevators are equipped with recording watt meters to enable smooth control of the amount of recycle material in the system. The ex-drier conveyor is also fitted with a weighbelt as an additional check.

The main control over recycle rate is accomplished using flaps in the undersize granule chutework from two of the coarse screens. Fine control is maintained by extracting a controlled amount of product from the plant using a variable speed weighbelt under the product screens. Excess product overflows back to the process via the recycle conveyor.

Product Free Acid

The client requires a product with a free acid content of less than 4.5% P_2O_5. In order to achieve this it is necessary to add a neutralising agent to the product. The agent will be applied as a powder to product granules in the neutralising drum. The neutralising agent is FCMP (fused calcium magnesium phosphate).

Effluents and Scrubbing

The reaction between rock and acid is only 60-70% complete as the slurry leaves the reactors and continues during granulation, drying and to a lesser degree during cooling. All process airstreams within the plant therefore have to be treated to recover fluorine which is evolved as the reaction continues. The quantity of fluorine allowed in the discharged gaseous effluent is maximum 4 kg/hour; this is somewhat more lenient than the Florida EPA regulations which would allow a 60 tph GTSP plant to emit a maximum of 2.16 kg/hr. However the design level of fluorine in gaseous effluent is 2 kg/hr.

Drier, cooler and general plant dedusting airstreams are all passed through cyclones to partially recover entrained dust before passing to the scrubber system. In view of the relatively large airflows involved three separate scrubbers have been provided as follows:-

- Reactor/Granulator
- Drier
- Cooler/Dedust.

Each scrubber is a void tower with a short section of floating ball packing between spray levels. The scrubbers all operate counter-currently with a high liquor circulation rate.

The scrubber blowdown from the common circulation tank (which is about 2.5% fluosilicic acid) is neutralised with lime before it is returned to the TSP reaction system where it is used to dilute the incoming 54% P_2O_5 phosphoric acid. Thus during normal operation the plant is liquid effluent free.

CONCLUSIONS

Although China has abundant phosphate rock reserves, it currently imports large quantities of P_2O_5 fertilizers because the existing P_2O_5 production capability within the country does not meet the demand for phosphate fertilizer. However, China is taking the necessary steps to develop its P_2O_5 industry and within the next few years a number of large scale GTSP plants will be constructed.

It is essential to test the phosphate rock at the feasibility study stage of a project to determine whether it is suitable to be processed in the Den route or the Slurry route for TSP production.

Our results show that some of the Chinese phosphates are suitable for both process routes. In which case the selection of the process route will depend on other factors such as whether the granulation plant is required to produce other products, for example NPK fertilizers, and whether the phosphate rock is provided dry or as a slurry.

These can be evaluated during a feasibility study. Our experience shows that on a case by case basis there is likely to be clear techno-economic basis for selecting either the Den or Slurry process.

Figure 1

Location of Chinese Phosphate and TSP Projects

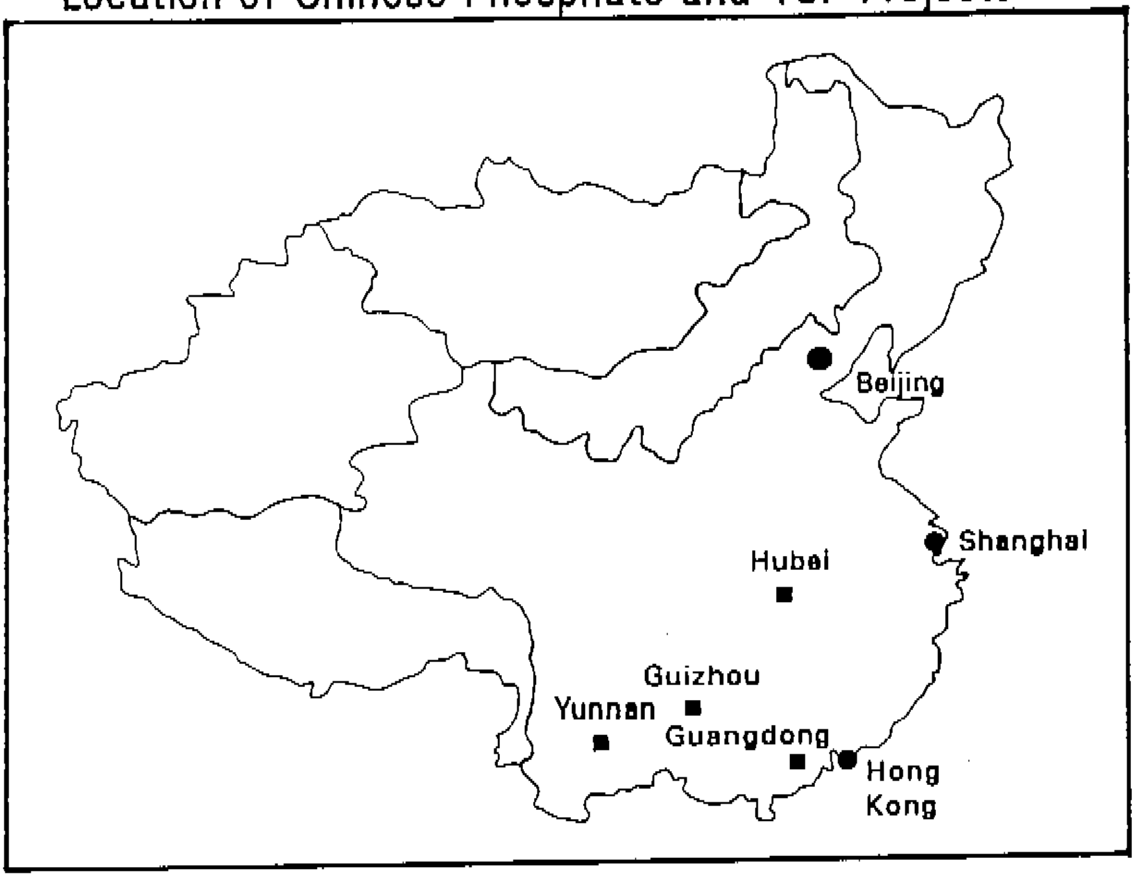

Figure 2

Comparison of Rock Reactivities

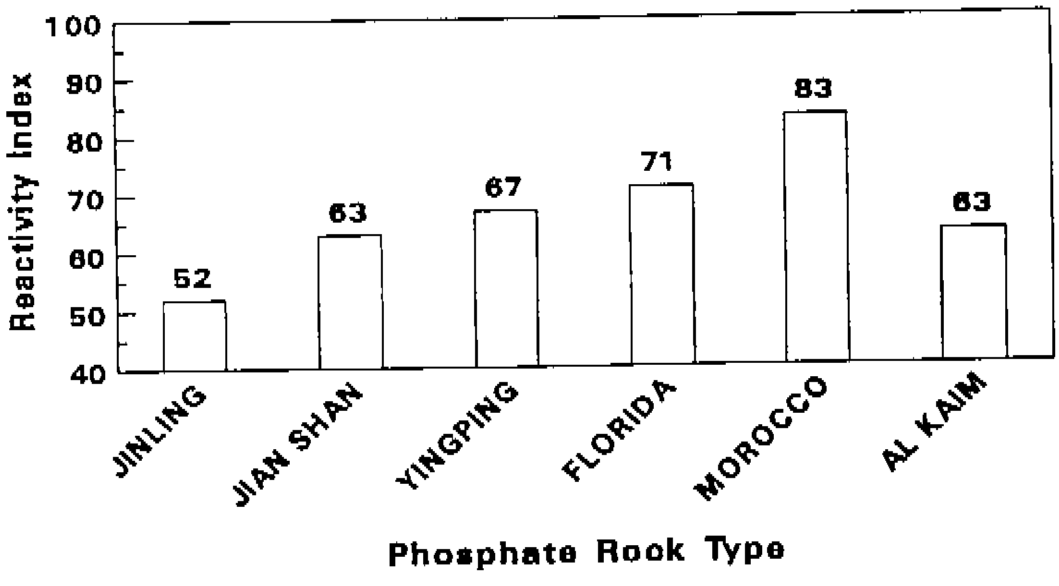

Fig. 3 TSP Product Quality - Dry Basis
Jian Shan Phosphate

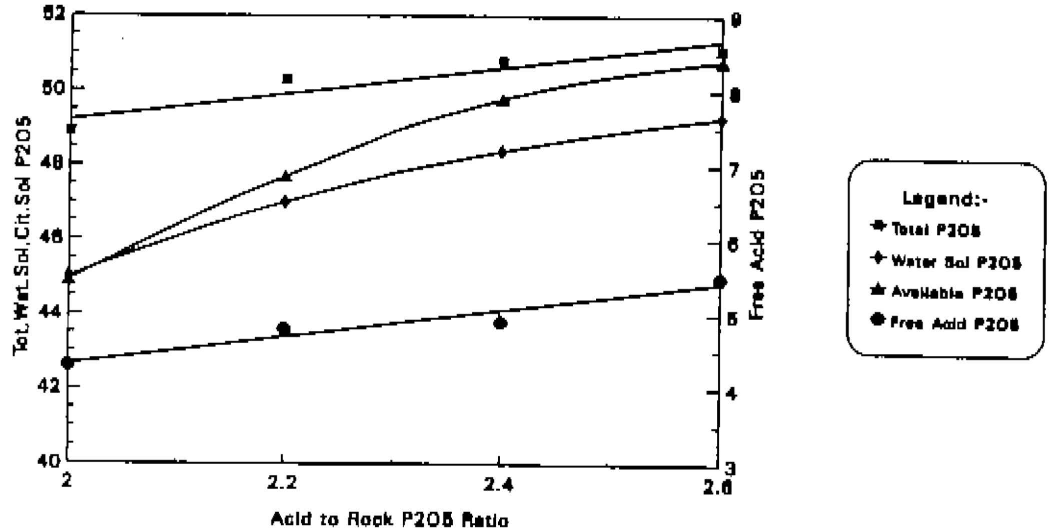

Fig. 4 TSP Product Quality - Dry Basis
Jinling Phosphate

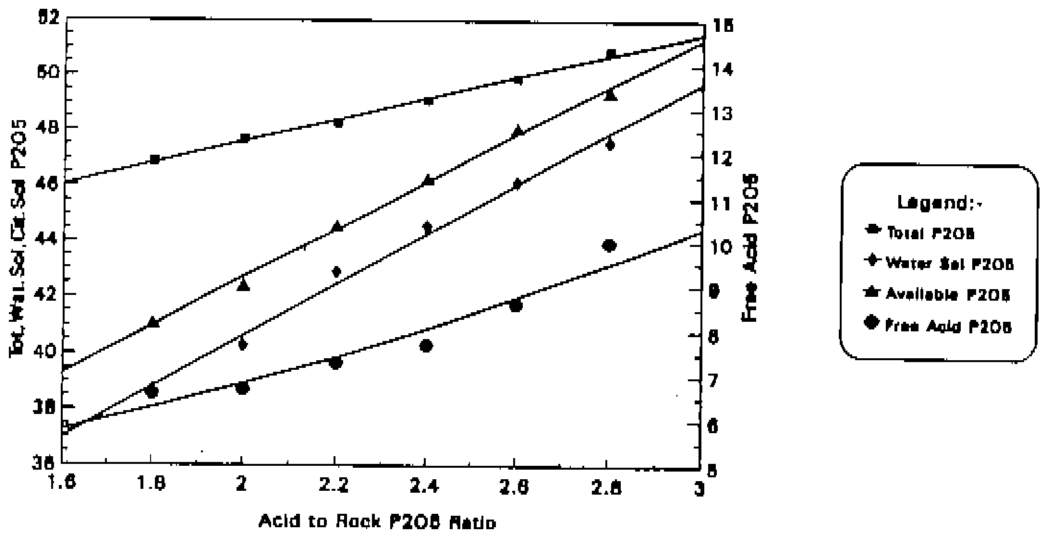

Fig. 5 TSP Product Quality -Dry Basis
Yingping Phosphate

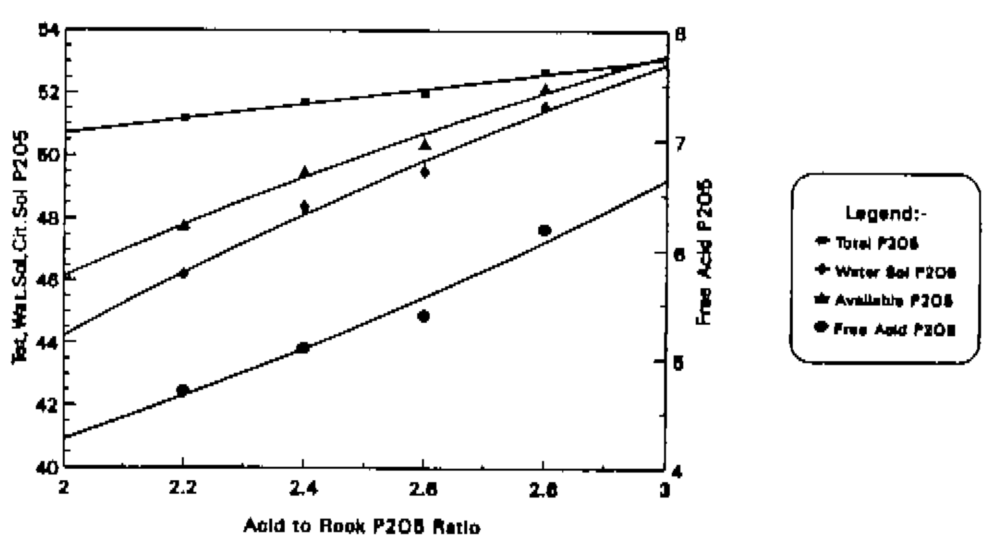

Figure 6

Slurry GTSP Process Flowsheet