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Design and Operating Data from the World's Biggest and Newest Hemihydrate Phosphoric Acid Plant

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En septembre 1999, la nouvelle usine d'engrais WMC Fertilizers de Queensland, Australie a été mise en service. Les équipements comprennent une unité d'acide phosphorique de 1 500 tpd P_2O_5, utilisant le procédé Hydro Hémyhidrate (HH). C'est la plus grande unité de HH construite en une seule fois.

L'exposé se concentre sur l'expérience d'exploitation de l'unité et discute des données-clés d'exploitation, y compris la qualité de l'acide, les émissions de gaz et la consommation d'énergie.

ABSTRACT

In September 1999, the new fertilizer factory of WMC Fertilizers of Queensland, Australia was started up. The facilities include a 1500 tpd P_2O_5 phosphoric acid plant using the Hydro Hemihydrate (HH) process. This is the largest single line grassroots HH plant in the world.

The paper focuses on operating experience with the plant and discusses key operating data, including acid quality, gaseous emissions and energy consumption.

Introduction

During 1999 and 2000 Hydro Fertilizer Technology, based in Brussels, Belgium, was involved in two projects to establish large scale phosphoric acid plants (2). Both these plants utilize the Hydro Hemihydrate (HH) process and were designed to supply downstream granular fertilizer units.

One of these projects was for WMC Fertilizers Pty Ltd. (WMCF), in Australia. This complex consists of a phosphate rock mine and facilities to produce ammonia, phosphoric acid and granular MAP and DAP at Phosphate Hill in Queensland, Australia. The facility was started up at end of September 1999, using sulphuric acid from a new plant 150 km away at Mount Isa, Queensland.

WMCF selected the Hydro HH process for the 1500 tpd P_2O_5 phosphoric acid plant. To date, it is the largest single line HH plant in the world and produces phosphoric acid at the concentrations required for downstream MAP and DAP processes. 40% P_2O_5 acid is produced directly from the filters, together with a 20% P_2O_5 side stream. Some of the 40% P_2O_5 acid is evaporated to 52% P_2O_5.

A description of the Hydro HH process is given at the end of the paper for the benefit of readers who are not so familiar with this process technology.

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All information given in the paper at the time of writing was obtained during the first 8 months of operation. An acceptance certificate for the phosphoric acid plant was issued in July 2000.

1. Background

The resource, which led to development of this project, is the Phosphate Hill phosphate rock deposit. This phosphate was first discovered by BH South in 1966. The total reserve (3) is expected to be 106 million tonnes, and the proven and probable reserve is 31 million tonnes averaging 21.5% P_2O_5.

In 1975 BH South established a phosphate rock mine, beneficiation plant, rail access to the coast and port facilities at Townsville. The operation was closed in 1978.

In 1980, WMC acquired BH South's interest in Phosphate Hill and other local reserves. During the 1980's, WMC resumed phosphate rock and continued to pursue various options for the development of the phosphate resource. Phosphoric acid and phosphate fertilizer options were examined and considerable laboratory and pilot plant scale test work was carried out in Hydro's laboratories (formerly Fisons) from 1981 through to 1999.

During the early 1990's, significant developments in North West Queensland together with a number of initiatives taken by the Queensland Government enabled WMC to secure commercial arrangements for the supply of natural gas and rail transportation which supported the development of an ammonium phosphate fertilizer project. In December 1996 the WMC Board gave approval for the Queensland Fertilizer Project to proceed. ITB documents were issued in June 1997 and a consortium of Mitsui Engineering and Shipbuilding / ABB / Clough (MAC) was formed.

An offer was made by MAC with Hydro technology for the lump sum turnkey contract for the phosphoric acid plant and the consortium secured the contract in September 1997. The time schedule for the contract was tight but construction was completed by July 1999.

Timing of the construction of the other turnkey plants at the site was not so advanced, so there was a delay until end September, when chemicals were first fed to the phosphoric acid plant.

2. Project Details

The phosphoric acid plant consists of the following unit operations:

Rock Filtration
Reaction
Filtration
Scrubbing
Product Storage
Acid Concentration

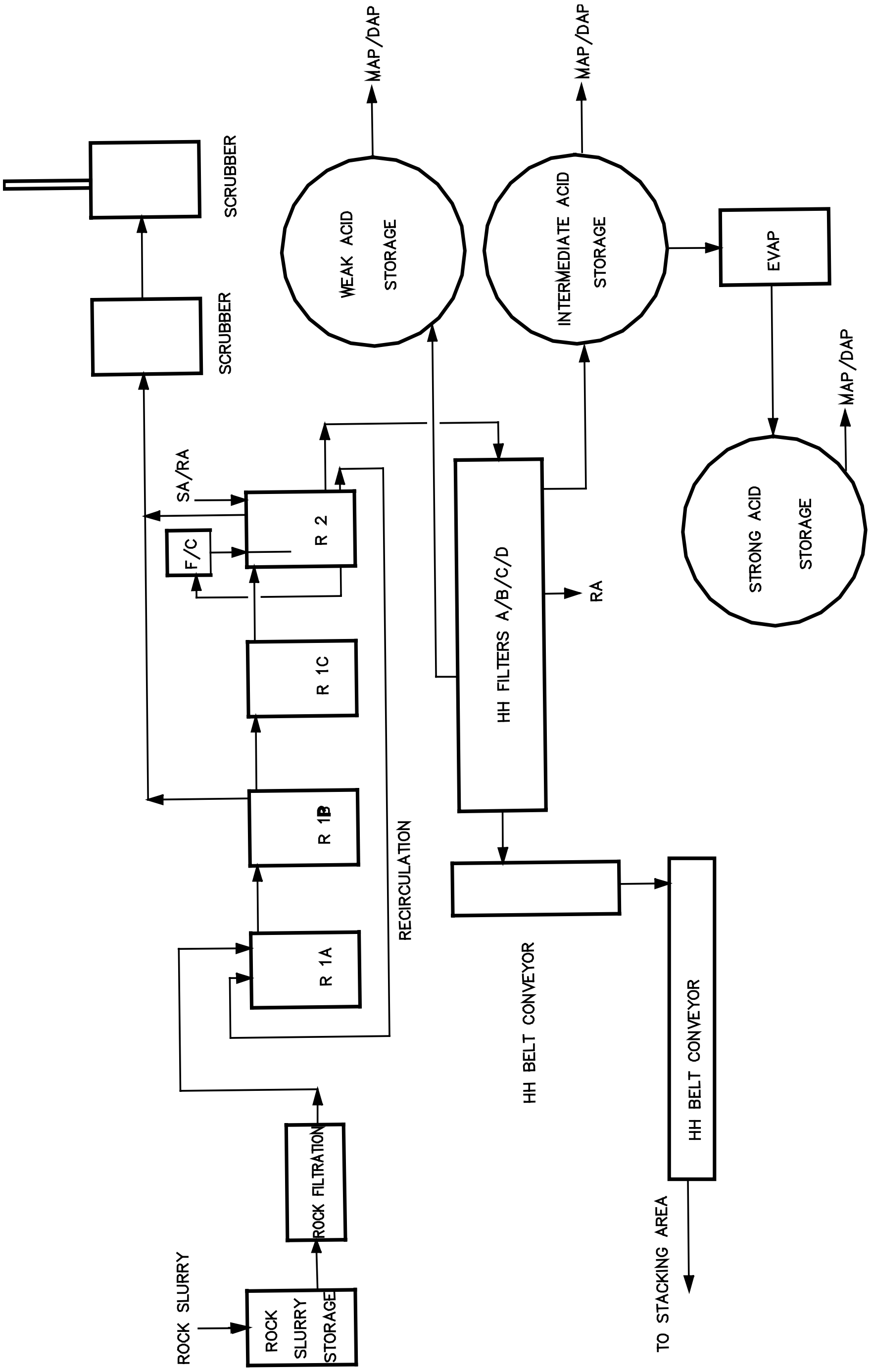
A conceptual layout of the plant is given in Figure 1, overleaf.

Rock Filtration

Raw phosphate rock is crushed and partially beneficiated by slurrying with water and removal of slimes.

Two belt filters (previously used in the mineral processing industry) were refurbished and installed at the site. These are used to de-water the phosphate rock prior to feeding it to the hemihydrate reaction section with a moisture content of 17% or less.

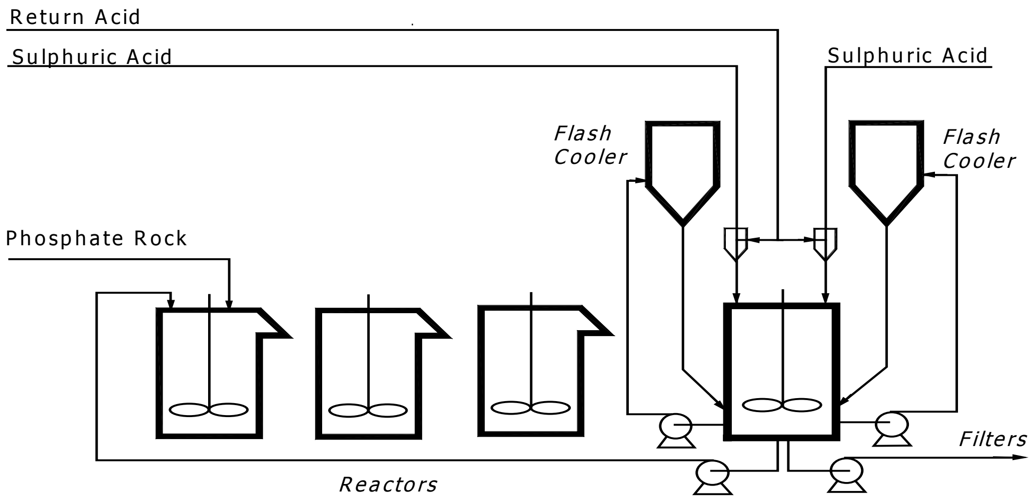
Figure 1: Conceptual Layout of WMCF Phosphoric Acid Plant



Reaction System

A diagram of the reaction system is given in figure 2.

Figure 2: Reaction System Details



The reaction system consists of four reaction vessels; each connected by an overflow launder to the next vessel. The first three of these (reactors 1A, 1B and 1C) are deficient in sulphate and are used to dissolve the phosphate rock in the phosphoric acid. The fourth vessel (reactor 2) has an excess of sulphate and is used to crystallise the dissolved rock in the form of calcium sulphate hemihydrate. Sulphuric acid is mixed with return phosphoric acid in two specially designed conical mixers. Without these mixers, uncontrolled crystallisation would lead to poor crystal formation in zone 2 due to localised areas of high sulphate concentration.

The phosphate rock contains almost 40% w/w silica. A significant proportion of the phosphate is found inside the silica particles. Therefore the volume (and thus residence time) of the sulphate deficient dissolution (digestion) zone was increased to allow sufficient time for the phosphate encapsulated in the silica to be dissolved. In this plant, the volumetric ratio of the dissolution zone to the crystalliser is 3:1. For most other phosphate rocks, the ratio is 2:1. However, the overall reaction volume and residence time was not increased from the standard.

There is a controlled recirculation of slurry from reactor 2 back to reactor 1A. This is important in maintaining the correct conditions for rock dissolution and hemihydrate crystallisation. Cooling of the reactor slurry is achieved by means of two flash cooler vessels which circulate slurry around reactor 2. Temperature of the slurry is controlled at 98 to 100 degrees C. The reaction slurry is composed of 41% P_2O_5 phosphoric acid and hemihydrate solids at around 30% w/w.

The high level of mainly inert silica in the phosphate rock caused the slurry in the reaction system to be highly erosive. Consequently, materials of construction were chosen for equipment coming into contact with the slurry, that would withstand the erosive forces. The reaction vessels are rubber lined carbon steel with carbon brick protection although reinforced concrete could have been used instead of carbon steel. The reactor slurry pumps are cast iron with neoprene rubber impellers and casing liners. The reactor agitators and slurry piping are Duplex stainless steel which is resistant to the highly erosive slurry. Flash cooler slurry piping is rubber lined carbon steel with carbon brick protection.

Hemihydrate Filtration System

Reaction slurry is fed to four horizontal belt filters. The product acid (over 40% P_2O_5) is removed and pumped to Intermediate acid storage. A weak acid stream (20% P_2O_5) is also removed and pumped to weak acid storage. This weak acid take-off was included at the request of the client. It is intended for use in the gas scrubbing system of a downstream plant. Filter cake washing is counter-current, with fresh water and the hemihydrate cake is discharged from the filters as a 'dry' solid onto a collection conveyor.

The four filters are arranged in groups of two independent pairs. Each pair share common return acid and product acid seal tanks. This allows for some flexibility in operation and washing procedures.

There is a large amount of unreactive silica (up to 40% SiO_2) in the phosphate rock which passes untouched through the reaction system and is deposited with the phosphogypsum as filter cake on the belt filters. As a consequence of this, the mass of filter cake is approximately 25% more than would be found with other commonly available rocks. Clearly this, and the presence of small silica particles, will affect the filter area requirement. For this project, a filtration rate of 4.4 tpd P_2O_5 / m^2 is installed. This compares with a more usual 7 to 9 tpd P_2O_5 / m^2 for most rocks processed in HH mode and >16 tpd P_2O_5 / m^2 for the igneous Jacupiranga (Brazil) rock.

Butyl rubber belts with natural rubber curbs are used for the filters with 904 L stainless steel receivers. Slurry piping is Duplex stainless steel and acid piping is fiber reinforced plastic (FRP). Water and process gas piping is also in FRP. Filtrate pumps are in neoprene rubber lined cast iron.

The hemihydrate from each filter is discharged to a collection conveyor and then transferred to an overland conveyor which discharges it into a slurrying tank. The hemihydrate slurry is discharged to the stack. Pond water is not returned to the process at present.

Scrubbing Systems

Reactor off-gases are collected and directed to the first stage scrubber. Here the gases are scrubbed in a void tower with cooling water (straight through basis) to remove majority of fluorine and silica present in the off-gases. They then pass to the second stage scrubber, where they are joined by filter off-gases and further scrubbed with cooling water prior to passing to atmosphere from the stack.

Gases from the filter vacuum systems and flash cooler vessels are also scrubbed with acidic cooling water. A cooling tower system is used to control the temperature of the water and there is a blow down to the gypsum stack area to limit the build-up of impurities in the cooling water circuit.

The scrubber vessels are in rubber lined carbon steel and water piping in FRP.

Product Storage

The three different strengths of phosphoric acid (weak, intermediate and strong) are stored in a total of seven tanks. Each tank is equipped with an agitator to maintain solids in suspension. There are no sludge removal systems, as the acid from hemihydrate process is of a suitably high quality with low solids content that it can be used directly in downstream MAP and DAP processes. A ring main system is used for transfer of acid from storage to the MAP/DAP plant.

The tanks are rubber lined carbon steel with acid lines in FRP. The storage pumps are neoprene rubber lined cast iron.

Acid Concentration System

Approximately half of the intermediate acid (720 tpd P_2O_5) is concentrated from 40% P_2O_5 to 52% P_2O_5 in a single vacuum evaporator unit. All vapours are absorbed by the cooling water in the condenser. Vacuum is supplied by a liquid ring vacuum pump and the strong acid product is fed to storage. Heating is by means of low pressure steam.

The heat exchanger consists of impregnated carbon tubes. The vacuum chamber is rubber lined carbon steel with carbon tile protection. The recirculation pump is constructed in Duplex stainless steel and the piping is a mixture of rubber lined carbon steel and 904 L stainless steel.

3. Operating Data

Raw Materials

Phosphate Rock

Duchess phosphate rock is an unusual deposit, dating from the Cambrian era, composed of ore averaging 17.5 % P_2O_5 (4) Selective mining, followed by crushing and desliming results in a product of approx. 23.5 % P_2O_5. Much of the P_2O_5 is encapsulated in a silica matrix, which must be broken down by grinding to 0.5 mm to assist in the liberation of the P_2O_5 from the mainly inert silica matrix. The level of SiO_2 in the rock can be up to 40%. An analysis of the rock (dry basis) obtained from WMCF (5) is given below in Table 1.

Table 1: Analysis of Phosphate Rock

Component	% wt/wt April 2000 ave	% wt/wt June 2000 ave
P_2O_5	24.63	22.23
CaO	34.45	31.32
SO_4	0.37	n.d.
Al_2O_3	1.03	1.10
Fe_2O_3	1.63	1.82
MgO	0.14	0.14
F	2.08	2.37
Cl	0.012	n.d
SiO_2	32.34	37.5
CO_2	1.13	1.00
C organic	0.31	0.27
Moisture	19.66	21.5

The phosphate rock is designed to be dewatered to < 17.0 % free moisture prior to being fed to the reaction system. The phosphate rock is ground during the beneficiation process to the design specification given in Table 2.

Table 2: Rock Size Analysis

Aperture (mm)	BSS No.	Typical wt % through
0.5	30	100
0.425	36	95.4
0.3	52	81.9
0.15	100	56.5
0.106	150	45.9
0.075	200	35.7
0.053	300	27.8

This is finer than the typical requirement of 100% below 2 mm for the HH process. This rock can be considered to be a high grade rock, diluted by the unreactive silica. Therefore the impurities are in relatively low concentration, so once processed, the resulting phosphoric acid is of a high quality. Furthermore, the hemihydrate process produces acid low in Al_2O_3 and SO_4. Typical analysis of filter acid is given in Table 3.

Sulphuric Acid

Sulphuric acid (98.5%) is obtained from the smelter at Mount Isa and also from Townsville. Transport is by rail in GAT-X rail wagons. One or two trains arrive at Phosphate Hill daily and are emptied into one of three storage tanks.

Actual Operation

The phosphoric acid plant started operation on 25 September 1999.

The start-up was from water (in the reactors) with phosphate rock and sulphuric acid being fed at 50% of design rate until stable operation was established. During the first phase of the start-up the intention was to produce gypsum in the dihydrate (DH) form until acid of approximately 30% P_2O_5 was achieved.

Acid at this strength produced from the filters was concentrated to approximately 40% P_2O_5 in the evaporator.

The start-up procedure was interrupted by stoppages in downstream plants.

When the phosphoric acid plant was restarted, operation was stabilised in DH mode then switched to hemihydrate (HH) operating conditions by increasing temperature, decreasing filter cake wash water flow (to increase the P_2O_5 concentration in the reactor) and decreasing the slurry recirculation flow.

A transition period of 68 hours of operation when moving from DH to HH conditions was required until the design flow of slurry to the two filters was achieved.

One of the HH filters was operated at 120% of its design load another 48 hours later.

Analysis of Acid and Hemihydrate

Samples of product acid from the HH filters and evaporator have been analysed by WMCF(5) and their results are given in table 3 below:

Table 3: Analysis of Phosphoric Acid

	Acid ex. Filters March 2000	Acid ex. Evaporator March 2000
Component	% wt/wt	% wt/wt
P_2O_5	39	51.4
CaO	0.23	0.05
SO_4	1.99	2.27
Al_2O_3	0.6	0.9
Fe_2O_3	2.81	2.7
MgO	0.23	0.25
F	1.23	0.41
Cl	158 ppm	18 ppm
SiO_2	0.57	0.11
Solids	0.16	3

The acid analysis is typical of that produced from the hemihydrate process. The sulphate level is under 2%, and the aluminium and solids are also low. The iron content in the ex-filter acid is higher than expected and this is due to the Fe_2O_3 content in the phosphate rock being higher than design.

The approximate distribution of the Al_2O_3, Fe_2O_3 and MgO between the ex-filter acid and the hemihydrate gypsum is as follows:-

	% in Filter Acid	% in HH Gypsum
Al_2O_3	30	70
Fe_2O_3	65	35
MgO	80	20

Samples of hemihydrate phosphogypsum have been analysed and the results are given in table 4 below:

Table 4: Analysis of Hemihydrate

Component	% wt/wt 01 – 02 May
P_2O_5	1.91
CaO	27.00
Al_2O_3 (total)	0.60
Fe_2O_3 (total)	0.45
MgO (total)	0.12
F	0.69
SiO2	24.9
Na_2O	0.17
K_2O	0.15

The high silica content shows that most of the silica in the rock has been unaffected by processing and reports to the hemihydrate. This silica has a diluent effect on the other elements. The phosphogypsum is stacked.

P_2O_5 recovery efficiency of 93 to 94% has been achieved but not on a continuous basis due to the high moisture in the rock feed which means that the filter cake wash water has to be reduced below the required amount for good washing characteristics.

Foaming

The phosphate rock contains a relatively low concentration of carbonate so the amount of foaming is not excessive. During operation as a DH plant, there were significant amounts of foam on the slurry surface. A defoamer (Struktol) was used to control this. When HH operation was commenced, the defoamer was turned off and since that time is rarely used. There is no significant gasification of the hemihydrate slurry. The surface foam is less than with DH operation.

Routine Shutdowns for Washing

Normally, as in most processes, the plant is shutdown on a regular basis to wash the filter systems and remove deposits of fluosilicate scale. The wash procedure was carried out every one or two weeks although there was little evidence of scaling. The use of a proprietary antiscalant prevented accumulation of calcium sulphate scale in the filters and associated equipment. The antiscalant has been very effective.

Experience has shown that the degree of fluosilicate scaling within the filter circuit has been small and the frequency of shutdowns for washing can be extended from once every week to once every 3 weeks.

Emissions

Measurement of the gas emissions from the gas scrubber stack has been carried out. A figure of 0.009 g HF/m^3 was obtained.

Utility Consumption

Consumption of electrical power has been measured at 4.6 MWh for the phosphoric acid plant.

Steam consumption in the evaporator has been measured at 0.65 t/t P_2O_5. Consumption within the phosphoric acid plant filtration systems amounted to 0.11 t/t P_2O_5. The steam supply was generated from the ammonia plant or from package boilers when insufficient steam was available from the ammonia plant.

4. Conclusions

This paper has given an insight into the start up and early operation of the largest single line grassroots hemihydrate phosphoric acid plant in the world.

The start up schedule was delayed and production limited by problems in the ammonia plant. However, operation of a major hemihydrate plant has been successfully established. Further improvements in efficiency are expected when the moisture content in the rock feed can be controlled below 17% free moisture.

References

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Process Description

The following descriptions of the hemihydrate processes are given for the benefit of those people not already familiar with these processes.

Phosphate rock is a complex material; the principal mineral constituent is fluorapatite which contains phosphate, fluoride, carbonate and other radicals bound together within a crystal lattice. When the rock is treated with a strong mineral acid, the apatite lattice is destroyed and the components pass into solution. In the wet phosphoric acid process the apatite is dissolved in a phosphoric acid solution and sulphuric acid is added to precipitate the calcium according to the following simplified overall reaction.

$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$ (1)

Various side reactions occur concurrently: the most important being the action of sulphuric acid on calcium fluoride and calcium carbonate.

$CaF_2 + H_2SO_4 = 2HF + CaSO_4$ (2)

$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4 + H_2O$ (3)

An overall reaction for the process may therefore be written as:

$Ca_{10}(PO_4)_6\ F_2\ CaCO_3 + 11H_2SO_4 + 11xH_2O =$

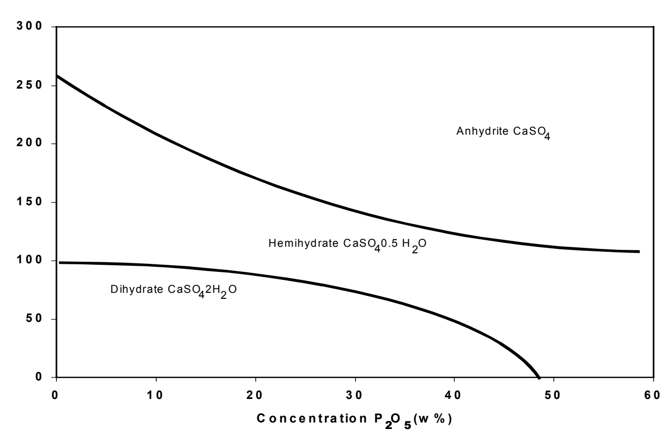
$6H_3PO_4 + 11CaSO_4XH_2O + 2HF + CO_2 + H_2O$ (4)

Depending on the reaction temperature and phosphoric acid concentration, the calcium sulphate formed in the reaction can be in three stages of hydration; anhydrite, hemihydrate or dihydrate (i.e. $CaSO_4.xH_2O$ where x = O, ½ or 2 respectively). This is determined in accordance with the phase diagram shown in Figure 3.

Figure 3

Effect of Reaction Conditions on Calcium Sulphate Crystallisation

It can be seen that, to produce calcium sulphate in the dihydrate form, conventional



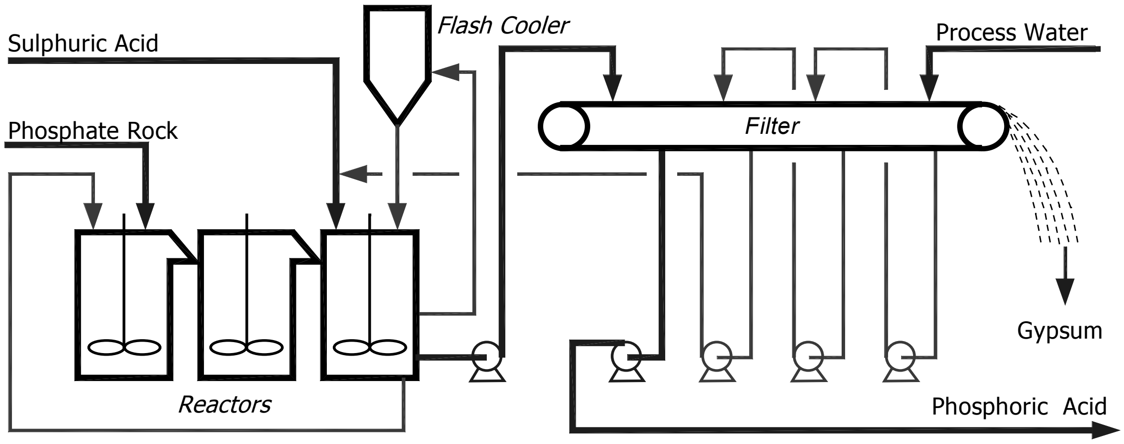
processes operate typically at $80^{O}C$ and 30% P_2O_5. Hemihydrate processes are controlled at $100^{O}C$ and 40 to 50% P_2O_5, so that a separate concentration stage may not be required and significant reduction in energy consumption is achieved. Furthermore, a number of unit operations necessary for a dihydrate process (e.g. intermediate acid storage and clarification) are avoided with the hemihydrate route.

Hemihydrate (HH) Process

The major operations involved in the HH process are shown in Figure 4. Reaction and filtration are the key process steps. The hemihydrate reaction proceeds in two distinct zones. It is therefore necessary to have at least two vessels or compartments. The preferred volumetric ratio of zone 1 to zone 2 is normally 2:1.

Figure 4

Hydro Fertilizer Technology Hemihydrate Process



Phosphate rock is fed to reaction zone 1 (first two vessels in figure 4), sulphuric acid and dilute phosphoric acid ("return acid" from the filter) are fed to reaction zone 2 (third vessel). Slurry from reaction zone 2 is recycled to reaction zone 1, thus exposing the phosphate rock to sulphate ions under controlled chemical conditions. Heat is removed by air or vacuum cooling to maintain the reaction slurry temperature at 98 to $100^{O}C$.

Acid can be produced directly from the filter at between 40 and 50% P_2O_5, depending on downstream requirements.

The product acid and hemihydrate are separated by a horizontal vacuum filter with counter current wash stages. The product acid from the filter passes directly to storage. It does not require clarification or solids removal.

The HH process is simple with only a few unit operations. It is especially suited to minesite operations where phosphate rock is readily available at a relatively low cost.

Hemidihydrate (HDH) Process

The HDH process is a development of the HH route whereby the P_2O_5 recovery efficiency is increased to 98.5% or more.

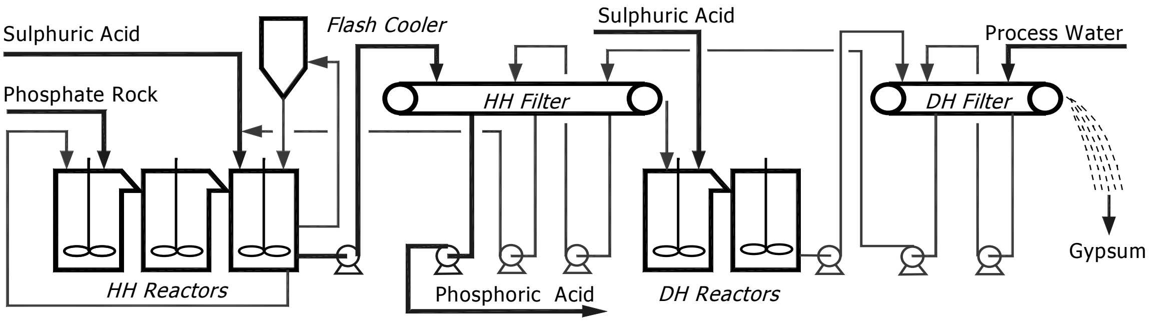
In the HH process, as in the dihydrate process, the P_2O_5 recovery efficiency is affected by co-crystallisation of phosphate in the calcium sulphate crystal lattice.

When phosphate rock costs are increased for example by the cost of transportation and handling, the lattice P_2O_5 loss from the phosphoric acid process can be reduced by using the HDH route. The HDH route is very appropriate as it reduces the lattice P_2O_5 loss significantly. This makes the HDH process particularly attractive for manufacturing locations remote from the source of phosphate rock.

A simplified flow diagram of the HDH process is shown in Figure 5.

Figure 5

Hydro Fertilizer Technology Hemidihydrate Process



The first stage of the process is almost identical to the HH process already described.

In the transformation stage the hemihydrate cake is discharged from the first stage filter into an agitated vessel, the first of two in series. The operating conditions are controlled to ensure complete transformation of hemihydrate to dihydrate and allow sufficient time for the dihydrate crystals to grow. The rate of transformation is increased by the addition of a small feed of sulphuric acid. Nearly all the lattice P_2O_5 co-precipitated with the hemihydrate is released into the liquid phase.

The dihydrate is then filtered and the cake washed with process or pond water. The filtrate containing the released P_2O_5 is returned to the hemihydrate reaction stage as the last wash on the hemihydrate filter.