Lecture 19  
Production Processes of Phosphoric acid

Five process routes are discussed in this section and these represent the principal process routes which are available.

2.3.1 Dihydrate process

This is the most diffused process and the advantages of dihydrate systems are:-

– There is no phosphate rock quality limitation
– On-line time is high
– Operating temperatures are low
– Start-up and shut-down are easy
– Wet rock can be used (saving drying costs)

The disadvantages are:-

– Relatively weak product acid (26-32% P₂O₅)
– High energy consumption in the acid concentration stage
– 4-6% P₂O₅ losses, most of them co-crystallised with the calcium sulphate

Diagram 1: Dihydrate Process

The dihydrate process comprises four stages: grinding, reaction, filtration and concentration

Grinding

Some grades of commercial rock do not need grinding, their particle size distribution being acceptable for a dihydrate reaction section (60-70% less then 150μm). Most other phosphate rocks need particle size reduction, generally by ball or rod mills. Both mills can operate with wet or dry rock.
Reaction

The tricalcium phosphate is converted by reaction with concentrated sulphuric acid into phosphoric acid and insoluble calcium sulphate. The reactor maintains an agitated reaction volume in circulation. The reaction system consists of a series of separate agitated reactors but in the interests of economy of materials and space, the multi-vessel reaction system is replaced by a single tank in some processes. Some of these single tanks may be divided into compartments which are virtually separate reactors. The operating conditions for dihydrate precipitation are 26-32% P$_2$O$_5$ and 70-80°C. This temperature is controlled by passing the slurry through a flash cooler, which also de-gasses the slurry and makes it easier to pump. The temperature can also be controlled by using an air circulating cooler.

Filtration

This stage separates the phosphoric acid from the calcium sulphate dihydrate. Five tones of gypsum are generated for every tonne (P$_2$O$_5$) of product acid produced. The filter medium must move in sequence through the various stages for continuous operation. The initial separation must be followed by at least two stages of washing, to ensure a satisfactory recovery of soluble P$_2$O$_5$. It is only possible to achieve the desired degree of separation at a reasonable rate if the filtration is either pressure or vacuum assisted and in practice vacuum is always used. The remaining liquid must be removed from the filter cake as far as possible at the end of the washing sequence. The cake must then be discharged and the cloth efficiently washed to clear it of any remaining solids which might otherwise build up and impair filtration in subsequent cycles. The vacuum must be released during the discharge of the cake and it is beneficial to blow air through in the reverse direction at this point to help dislodge the solids. The filtrate and washings must be kept separate from one another and have to be separated from air under vacuum conditions and then delivered under atmospheric pressure, as product, or for return to the process. The pressure difference is usually maintained by delivering the filtrates below the surface of the liquid in barometric tanks placed at a level sufficiently below the separators for the head of liquid to
balance the vacuum. The most common filtration equipment is of three basic types: tilting pan, rotary table or travelling belt.

**Concentration**

There is a long history of direct contact concentrators, in which evaporation is effected by bringing the acid into intimate contact with hot combustion gas from a burner, enabling equipment walls to be made of materials and in thicknesses which are suitable for efficient indirect heat transfer. Various patterns of direct-fired concentrator have been devised. Currently, almost all evaporators that are being built today for this service are of the forced circulation design.

The forced circulation evaporator consists of a heat exchanger, vapour or flash chamber, condenser, vacuum pump, acid circulating pump and circulation piping. A fluosilicic acid scrubber is usually included in the forced circulation evaporator system. All the evaporators in this service are generally of the single-effect design because of the corrosive nature of phosphoric acid and the very high boiling point elevation. The heat exchangers are fabricated from graphite or stainless steel with the rest of the equipment made from rubber-lined steel. All equipment designs will be made using the best practices of engineering available. More than one evaporator may be used, with the acid passing in sequence through each, depending on the degree of concentration required.

**2.3.2 Hemihydrate (HH) process**

Operating conditions are selected in this process so that the calcium sulphate is precipitated in the hemihydrate form. It is possible to produce 40-52% P₂O₅ acid directly, with consequent valuable savings in energy requirements. The stages are similar to those of the dihydrate process but grinding may be unnecessary.

The main advantages of this process, apart from the reduction or elimination of evaporation heat requirement, are:-
Capital savings.

Purer acid.

Acid from the HH process tends to contain substantially less free sulphate and suspended solids and lower levels of aluminium and fluorine than evaporated dihydrate process acid of the same strength.

Lower rock grinding requirements.

A satisfactory rate of reaction can be achieved from much coarser rock than in the dehydrate process, because of the more severe reaction conditions in the HH process.

The disadvantages of HH systems are:-

Filtration rate.

Hemihydrate crystals tend to be small and less well formed than dihydrate crystals and thus hemihydrate slurries tend to be more difficult to filter than dihydrate slurries unless crystal habit modifiers are used to suppress excessive nucleation. With a good HH process however, there is no need to use crystal habit modifiers. There are examples of phosphate rocks that produce hemihydrate crystals achieving higher filtration rates than obtained with dihydrate crystals.

Phosphate losses.

Water balance considerations restrict the amount of wash water that can be used. At the same time, the amounts of both soluble and insoluble P$_2$O$_5$ remaining in the filter cake are greater because of the higher P$_2$O$_5$ concentration of the slurry being filtered. Nevertheless the simplicity of the HH plant and the absence of silicofluoride and chucrovite scaling in the HH filter, may compensate for the higher insoluble P$_2$O$_5$ loss via HH cake.
Scaling.

Hemihydrate is not a stable form of calcium sulphate and there is a tendency for it to revert to gypsum even before the acid has been filtered off. The conditions are even more in favour of rehydration during washing. In a good HH plant there is no conversion in the reactor battery. A small quantity of anti-scale agent may be required in a single-stage HH plant filter to avoid scaling.

Filter cake impurity.

The cake is more acidic than gypsum filter cake because of the extra P₂O₅ losses and it also contains more fluorine and cadmium.

Corrosion.

The demands on susceptible items of equipment, particularly agitators and slurry pumps, are increased because of the higher temperature (100°C) and acid concentration (40-50% P₂O₅) compared to a dihydrate plant.

2.3.3 Recrystallisation processes

The best P₂O₅ recovery efficiencies that generally can be expected in the single-stage dihydrate and hemihydrate processes considered so far, are 94-96% and 90-94% respectively. The P₂O₅ losses are retained in the filter cake and this can create problems with disposal or use of the by-product gypsum. Some of this loss of P₂O₅ passes into solution and can be recovered when the calcium sulphate is finally separated, if the calcium sulphate is made to recrystallise to its other hydrate. This not only raises the overall efficiency of the process but also gives a much cleaner calcium sulphate.
Several processes have been developed but there are only three basic routes:-

– Acidulate under hemihydrate conditions; recrystallise to dihydrate without intermediate hemihydrate separation; separate product. (Hemihydrate recrystallisation (HRC) process)

– Acidulate under hemihydrate conditions; separate product; recrystallise hemihydrate to dihydrate; filter and return liquors to process. (Hemi-dihydrate (HDH) process)

– Acidulate under dihydrate conditions; separate product; recrystallise hemihydrate; filter and return liquors to process (Dihydrate-Hemihydrate (DH/HH) process)

2.3.3.1 HRC process

The flow diagram of this process resembles that of the multiple reactor dihydrate process with the exception that the attack reactor operates under hemihydrate conditions, while succeeding reactors operate under conditions favouring the rehydration of hemihydrate to gypsum. This is encouraged by seed dihydrate crystals recycled in the slurry from the filter feed. The product acid is no more concentrated than that obtained from dihydrate but the gypsum is much purer.

2.3.3.2 HDH process

It is possible to obtain 40-52% P₂O₅ acid directly, by acidulating under hemihydrate conditions and separating the hemihydrate before recrystallising, in this process. The additional filter and the other equipment required, add to the capital cost of the plant but enable savings to be made on evaporation equipment.
2.3.3.3 DH/HH process

In this process, although the reaction runs under dihydrate conditions, it is not desirable to effect a very high degree of P₂O₅ recovery during the separation of the acid from the dihydrate. The succeeding dehydration stage requires around 20-30% P₂O₅ and 10-20% sulphuric acid. The strength of the product acid is 32-35% P₂O₅.

2.3.4 Repulping process

A further optimisation of the HRC process can be obtained by re-slurrying and washing the gypsum, followed by a second filtration step in the so called “Repulping Process”. Most of the free acid which is not removed in the first filtration step, can be removed in this process and the efficiency can be improved by up to 1% (depending on the amount of free acid). The gypsum from the first filter is re-slurried in a tank and then pumped to a second filter where the gypsum is de-watered. The gypsum is then washed with the fresh water coming into the plant. The liquid obtained from the second filter is used on the first filter to wash the gypsum. The repulp process is in fact an additional step in the counter-current washing of the gypsum using the water that enters the plant.