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### THE STARTING-UP OF A PHOSPHORIC ACID PLANT, WORKING ACCORDING TO THE DIHYDRATE PROCESS.

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#### Design of a Phosphoric Acid Plant

A modern phosphoric acid plant, making use of phosphate rock and sulphuric acid as raw materials, and producing in addition to phosphoric acid, calcium sulphate in the form of dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , may be designed in different ways, but the works of different designers will have much in common. The chemical process is the same as are the conditions for making good calcium sulphate crystals which can be readily filtered. These conditions will necessitate the same temperatures in the digesters and the same range of concentrations for the mother liquor. It will be necessary in addition to circulate a certain amount of phosphoric acid in the process, usually by adding wash liquid but also by circulating sludge.

As a modern phosphoric acid plant works continuously and is wholly mechanised, every plant will have an apparatus for the automatic weighing of ground phosphate and also means for measuring sulphuric acid and the circulating phosphoric acid in a continuous or intermittent way. If the phosphate is weighed and the acids are measured intermittently in portions, accuracy will be increased, which will be favourable to the formation of the calcium sulphate crystals and indirectly to the filtration speed.

The main reaction takes place in digesters, which are usually three in number, each fitted with an efficient agitator. From the third digester or from a fourth vessel, acting as buffer between the two main parts of the plant, the digesters and the filters, the sludge is removed for filtration.

In order to obtain a product of concentration about 30%  $\text{P}_2\text{O}_5$ , the filtration should be performed on a horizontal filter. There are different types of horizontal filters, the rubber belt filter, the tray-belt filter and the disc filter. We do not want to discuss the merits of these varying types, as the problem of starting filtration, although in varying degree, will show the same difficulties.

There may be a difference in design in the method of mixing the raw materials and the circulating phosphoric acid, also a difference in the quantity of sludge or even in the quantity of phosphoric acid

circulating in the process. We do not think that this will influence the conclusions which we have arrived at regarding the starting up of a phosphoric acid plant.

Nevertheless, we should like to stress that our statements refer to a plant of a simple design, well known to us. Both the weighing of phosphate rock and the measuring of acids are carried out intermittently. The phosphate is mixed with the circulating acid, which has a concentration of 18 - 20%  $P_2O_5$ . This mixture is poured in portions into the first digester, where the sulphuric acid is added, as later described. From the third digester the sludge is conveyed to a fourth vessel acting as a buffer and from there to the filter or filters, either of the rubber belt or of the tray-belt type. The capacity of these filters should be large enough to give a certain margin for the time of filtration, so that the digesters will work all the time whilst the filters operate only part of the time. Using high grade Morocco or Pebble phosphate, the first filtrate from the filters will have a concentration of 30-32%  $P_2O_5$ , the second 18-20% and the third of about 5%  $P_2O_5$ . The second filtrate is returned to the process as circulating acid in a quantity ranging from 1.2 to 2.0 litres per kilo of phosphate rock, which means that the proportion of  $P_2O_5$  in the circulating phosphoric acid to the quantity of  $P_2O_5$  in the product will be from 0.9 to 1.5

#### Preparations for starting a plant.

There are always difficulties connected with the starting of a chemical plant. One plant is very seldom a direct replica of another having features of its own which have to be discovered. Its mechanical devices should be tried out very carefully before the actual start takes place. It should be checked that all parts needing acid-proof protection have such protection and that there is no leakage from vessels or pumps; this should be ascertained by working the plant with water. It is much easier and will save much trouble if this is carefully checked beforehand.

The production of phosphoric acid according to the dihydrate method is indeed no difficult process but requires a certain amount of control. There should be a means of measuring the temperature of the sludge and the concentration of its mother liquor at all vital points and also of determining the specific gravity of the filtrates. There should be a laboratory filter ready for speed tests and a microscope to study the form and size of the crystals. There should be a possibility of carrying out daily analyses of the  $P_2O_5$  in the raw material, of the  $P_2O_5$  and  $SO_3$  in the product, and of the total and water-soluble  $P_2O_5$  in the gypsum cake. Indeed these latter analyses should be made on average samples of the gypsum cake for every 8 hour shift during the starting period.

Diaries should be started from the beginning and someone should be appointed always to keep them up to date. In these diaries should be entered notes regarding temperatures and concentrations made hourly by the workers, results of filter tests, daily analyses and quantities of raw materials; the yield of attack and the total yield, calculated on the basis of analyses of insoluble and water-soluble  $P_2O_5$  in the filter cake, should be noted every day. Once a week a balance of the ingoing and outgoing  $P_2O_5$  should be established so as to trace hidden losses of  $P_2O_5$ . No phosphoric acid plant can be put into action with good results if these matters are not properly attended to.

The staff necessary for the supervision of the plant should be appointed before the actual start. A phosphoric acid plant generally works for 24 hours, 6 days a week. The number of workers for each shift depends on the size and design of the plant, but at least during the starting period there should be one foreman for each shift and a chemical engineer, whose only task should be to keep

the plant in running order. These persons should not be troubled with carrying out analyses or writing reports. There should also be skilled workers at hand to be called in for minor repairs, if necessary.

If the art of making phosphoric acid is new to the works, where the plant has been installed, the starter of the plant will have a two-fold task: he will have to start the plant with unskilled labour and have to teach everybody his special duty. This means in fact, that the plant will not work well until the whole personnel has been properly trained. The same difficulty will arise also when starting other chemical plants, which will account for the delay often encountered in these industries in arriving at normal conditions. Buyers of plants do not always recognise this fact. We have had to tell them: buying a phosphoric acid plant is like buying a piano; you will have to learn how to play it.

#### Putting the plant into operation.

A phosphoric acid plant can be started with water instead of with circulating phosphoric acid, but it will be easier to reach normal conditions if phosphoric acid is available.

The start can be arranged as follows. The first digester is filled about one third full with water/ or phosphoric acid/. The water or acid should, if possible, have a temperature of about 80°C, which will greatly facilitate the start, even with water. The automatic feeding apparatus is put into operation at its highest speed in order to increase the temperature as rapidly as possible. A mixture of ground phosphate rock and water/or phosphoric acid, is fed into the digester in portions, and at the same time the corresponding quantity of sulphuric acid is added via a leaden pipe at the bottom of the digester.

The best crystals are obtained at a temperature of about 80°C with a mother liquor of about 30-32% P<sub>2</sub>O<sub>5</sub>. It is evident that a lower temperature and a lower concentration of mother liquor will give smaller crystals, less easily filterable. Starting with water, the crystals will probably give a sludge with such low filtration rate that it will be necessary to stop the feed before the filtration is started.

If the plant is started on water, the filtration will result in a phosphoric acid of a comparatively low concentration. It will probably not be possible to wash out all phosphoric acid at this first filtration so there will be a certain loss.

The next step will be to start the reaction again by one third filling the emptied first digester with made acid, heating it if possible, and then starting the feeding as before. When starting the plant, the quantity of circulating acid/or water should be about 2 litres per 1 kilo phosphate rock. This time the crystals will be better and the filtering easier. The same procedure should then be repeated until an acid of 20% P<sub>2</sub>O<sub>5</sub> is obtained. A continuous process should then be attempted, with simultaneous reaction and filtration.

#### Main difficulty

The main difficulty is to obtain satisfactory crystals as soon as possible and to maintain them in a satisfactory condition.

The improvement in the size of crystals is dependent on the rise in temperature, the latter depending on the heat of reaction. The quantities of raw materials which must be treated per hour to give a sufficient rise in temperature and the quantities

needed to maintain the temperature at about 80°C can easily be determined. The automatic feeders can be regulated accordingly, and with such phosphates as high-grade Morocco or Pebble at least, the result will be satisfactory, easily filterable crystals.

Feeding in such proportions will only be possible if all the sludge produced can be filtered. As mentioned before, a certain loss of phosphoric acid may be permitted at the start, but should not be allowed under normal conditions. The reaction and the filtration are dependant on each other: the crystals must be satisfactory enough to allow quick filtration, and the filtration rapid enough to allow a high temperature to be reached by rapid feeding.

This is rather unfortunate. If anything goes wrong with the filter so that filtration has to be stopped for a few hours, the buffer vessel will be filled up and the feeding of raw materials has to be stopped. Then the reaction temperature falls and when the feeding starts again the crystals formed will be of smaller size. The reaction speed will be lessened and the filtration speed slowed down. Soon the feeding has to be stopped again with a still lowered temperature and still smaller crystals as a consequence. When this stage has been reached the plant must be stopped and then started again.

#### Temperature control.

There is no need to have this difficulty. If the temperature in the first digester is always kept at about 80°C., the crystal growth will not depend on the feeding speed. This can be arranged by a heating and a cooling device.

If steam is available, a steam coil should be installed in the first digester. This coil should be made of steel or copper, covered with homogeneous lead. If heated air is available, for instance from the cooling of pyrites furnaces, a Dow-therm installation could be used. The air heats a liquid with a high boiling point and this liquid circulates through the coil in the digester.

The Dow-therm liquid should never be allowed to circulate through a leaden coil in the digester. The lead will break sooner or later and the liquid will be lost.

There are other difficulties with a Dow-therm installation. The freezing point of the liquid is as high as +10°C. so that at lower atmospheric temperatures the circulation must be kept going. If the circulation pump stops, the liquid will freeze in the pipes and cause a great deal of trouble.

In a plant of normal size having its digesters isolated, no additional heat will be needed when the plant is functioning normally; when starting the plant after the week-end stop, the amount of heat to be added will be small. Consequently we propose that the heating should be done electrically, even in countries where the price of power is comparatively high.

In a plant with a comparatively high production, the temperature may rise too high so that the sludge has to be cooled. At a temperature of about 85°C. the formation of unstable hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ , will commence. This hemihydrate will take up water on the filter, forming dihydrate and causing the cake to harden. The cooling may be effected in different ways. The simplest will be to blow in air from a ventilator through a pipe 200-300 mm. diameter immersed to about 100 mm in the sludge of the first digester.

It should be noted that the temperature should be taken in the overflow from the first to the second digester.

In each shift a man should be employed solely for the regulation of the temperature during the starting period, maintaining it as constant as possible at about 80°C., which has been found to be the optimum value for the phosphate rock used. It will be possible to do without this man if an automatic temperature control is arranged.

#### Circulation of sludge.

We have been asked if sludge from the last digester should be returned to the first digester.

Our answer has been that inferior crystals give rise to inferior crystals and satisfactory crystals to satisfactory crystals. If the crystals are inferior the sludge should not be returned. If the crystals are satisfactory they will be better still if they grow on crystals already formed.

If a quantity of sludge is returned from the last to the first digester, the surface of the crystals available for precipitation of calcium phosphate is enlarged and at the same time the sulphuric acid added in the first digester is dispersed throughout the system. By this circulation the temperatures in the digesters can be kept at about the same level, which will improve the yield of attack.

For starting after the week-end stoppage, we recommend having the first digester half filled with sludge, which should be previously heated to 80°C. This necessitates the agitator in this digester running over the week-end.

#### Elimination of froth.

Great difficulties have arisen from the formation of froth to such an extent that it was believed, for some time, that certain phosphates were unsuitable for the production of phosphoric acid.

Frothing has two causes: the gases developed during disruption, carbon dioxide and hydrofluoric acid, and the organic matter in the phosphorites, which increases surface tension. Phosphates rich in carbonates and organic matter such as Gafsa and other North African phosphates will develop more froth than other phosphates.

It is known that phosphates rich in organic matter have been calcined in order to destroy this before they have been used as raw material for the making of phosphoric acid.

There is no need for such measures. Effective de-frothing can be arranged in the following way: on a vertical shaft immediately above the surface of the first digester is placed a rapidly rotating device of almost any shape. Its simplest form will be a vertically placed circular loop made of an 1/2" acid proof steel rod. The diameter of the loop can be about 300 mm. This device effectively destroys all froth on the surface of the digester even if Algerian or Tunisian phosphates are being used.

#### Filtration.

By the measures proposed by us we have succeeded in dividing the plant into two parts working separately. With a temperature control there is no longer the need for speeding up filtration in order to maintain the temperature of the sludge. On the contrary, the feeding can be regulated to follow the filtration speed, keeping the buffer vessel empty for emergencies. If a longer stop in the filtration becomes necessary, for instance for the changing of the filter cloth, the feeding can be stopped for a long time and then started again, and the crystals will still be satisfactory.

This will greatly facilitate filtration, which is the difficult part of the process. Crystals formed of the same materials in the

same proportions at a constant temperature will also result in a constant filtration speed. Once the most suitable thickness has been achieved, the thickness of the filter cake should also be kept constant, which can be attained by a back-flow for the sludge brought on the rubber-belt filters and a device for constant feeding for the tray-belt filters.

This means that with a constant speed of the rubber belt or the tray-belt, the mother liquor will be sucked off at about the same point and the same will occur with the wash liquids, so that there will be no necessity for shifting the point for adding the wash liquids or their volumes. In this way it will be much easier to arrive at an almost complete removal of the cake by washing.

The means of regulating the filter are: speed of belt, vacuum, thickness of cake, point of adding wash liquids, volume of wash liquids. The higher the filtration speed, the thicker the cake should be, which will facilitate a satisfactory removal by washing. There are plastic cloths, which will permit a sludge temperature of 80°C. A high temperature will give a high filtration speed. If steam is available, it will pay to heat the wash liquids.

On rubber-belt filters the thickness of the cake is limited, as the up-standing edges of the rubber belt have a maximum height of 100 mm. If the sides of the belt are turned up so that the belt forms a trough, the washing in the centre will be less satisfactory as compared with the sides. For a complete washing-out the tray-belt filter is preferable. The surface of the cake should always be covered with liquid.

Supervision of the filtration needs intelligence and care, and the workers should be selected on this basis. Sampling of the gypsum should be performed in such a way that the analyses will show the actual loss.

#### Hidden Losses

There is a loss of  $P_2O_5$  that is inevitable. The disruption of the apatite molecule in the dihydrate process is never complete. The yield after a 10 - 12 hours reaction will be about 96 - 97%.

Theoretically the efficiency of removal can be 100% but in reality there will be a small quantity of water-soluble  $P_2O_5$  left in the cake. The daily total yield will be shown by the analyses of the cake and should be noted in a diary.

The weekly balance of  $P_2O_5$  in and out of the plant, will show a lower yield than shown by the daily analyses in most plants. We have found that such hidden losses will sometimes surpass the losses shown by the analysis of the cake so that the total yield becomes only 80 - 90%.

There is only one way of preventing these losses, namely never to allow any spill-water to escape from the plant. The floors of the plant should be covered with acid-proof asphalt and drainage arranged, by which all spill-water is conveyed to a well lined with lead in the ground-floor. There should be no outlet from this well. Its content should be pumped up to a vessel above the filters and used as a wash liquid. The wash liquids on the filter would then be three: 5% filtrate, liquid from the well, and pure water.

If the well is not properly attended to, it will fill up and the ground floor be flooded. This, at least, will catch the eye of the worker.

It may seem to our audience that this would be a rather drastic measure. We have found, however, that negligence and unwillingness to follow the instructions given, are the worst enemies of a phosphoric acid plant. In an Italian installation inspected by us, a

well had been arranged in the bottom floor but this well had had an overflow to a near-by river. We found the well filled up to the over-flow with a liquid containing 20%  $P_2O_5$  passing out through the over-flow to the river and then out to the Mediterranean. This was attributed to "something being wrong with the filters."

#### Use of low-grade phosphates

As already mentioned, low-grade North African phosphates such as Gafsa have been considered unsuitable as raw materials for the production of phosphoric acid, the main difficulty being frothing. With the de-frothing device already described, frothing will give no trouble, but the acid should be dispersed on the surface of the first digester. If added at the bottom, the whole digester will be filled with a bubbling mass of froth.

The gypsum crystals can be formed in a size to permit filtration, but the temperature limits are narrow and a few degrees below the optimum temperature will affect the crystals. A temperature control, with means of heating or cooling the sludge, will be an absolute necessity. The plant should be started on a high grade phosphate and when the crystals are satisfactory, this phosphate can be substituted by a low grade.

We hope later to have an opportunity of submitting a report on the starting up of a phosphoric acid plant working according to the anhydrite process.