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**THE FIRST INSTALLATION
OF A PHOSPHORIC ACID
PLANT ACCORDING TO THE
ANHYDRITE METHOD AT
VERCELLI, ITALY.**

by

**SVEN NORDENGREN, ITALO FRANZIA
and ROLF NORDENGREN.**

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THE FIRST INSTALLATION OF A PHOSPHORIC ACID PLANT ACCORDING TO THE ANHYDRITE METHOD AT VERCELLI, ITALY

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Earlier Work

Nearly 30 years ago, in 1926, one of us started to investigate the process of making phosphoric acid out of phosphate rock and sulphuric acid. Owing to lack of high-grade phosphate rock at that time it was hoped to make a phosphoric acid by a direct process, containing about 30% P_2O_5 , which could be mixed with the sulphuric acid in the ordinary superphosphate process, thus increasing the amount of phosphoric acid in the product.

At that time phosphoric acid was being produced with a concentration of only about 20% P_2O_5 . The sludge obtained in the reaction was passed through a series of decanters meeting the wash liquids. No increase of the phosphoric acid concentration was possible by this method.

The investigation at Landskrona first led to a study of the crystal water content of calcium sulphate. This compound takes up crystal water according to the following formulae: $CaSO_4 \cdot 2H_2O$ (dihydrate) and $CaSO_4 \cdot \frac{1}{2}H_2O$ (hemihydrate). Further, there are crystals formed containing no water, $CaSO_4$ (anhydrite).

These crystal forms have been studied by the famous scientist J. H. van't Hoff⁽¹⁾. He used saturated solutions of sodium and magnesium chloride at different temperatures into which calcium sulphate was mixed. The experiments showed that the crystal forms of calcium sulphate are intimately connected with the vapour pressure of the crystal water. If the tension of the crystal water is greater than the vapour pressure of the solution, part or all of the crystal water will leave the calcium sulphate. On the other hand, if calcium sulphate in anhydrite form is introduced into a solution of sodium chloride of lower temperature, then the calcium sulphate will recrystallize and take up water.

During the research work at Landskrona it was found that the same reactions would take place if phosphoric acid was used instead of the sodium chloride solution. It was also found that crystalline forms with a lower content of water than $2H_2O$ could be obtained, having different degrees of stability. The more stable forms would permit of washing on filters, whilst the unstable forms took up more

(1) Zeitschrift für Physikallische Chemie, XLV 1903, page 257.

crystal water during this process. In this way we were able to explain not only why the sludge of phosphoric acid and calcium sulphate sometimes hardened on the filter making washing impossible, but also to find how an easily filterable sludge could be formed.

The results were specified in two patents corresponding to British patents 314,976 and 314,977, both with convention date July 7th, 1928⁽²⁾. In the first of these patents the rights are reserved for "Depositing the calcium sulphate substantially as CaSO_4 (anhydrite) or in a form in which the maximum water of hydration is corresponding to the formula $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$."

This is the first mention of the anhydrite process.

The second patent describes the hemi-hydrate process in which the reaction takes place in an autoclave. A small plant was built at Landskrona according to this method where it worked for several years. A preheated mixture of sulphuric and phosphoric acid was fed into the autoclave and ground phosphate rock was added, after which the vessel was closed. Owing to the reaction heat the temperature rose to 135°C and the autoclave developed pressure. The attack yield was very high, more than 99%, and the greater part of the calcium sulphate was crystallized as hemi-hydrate in a stable and easily washable form.

There were others at that time also working on the problem of making improvements in the phosphoric acid process. A company called the Kunstdünger Patent Verwertungs A.G. with laboratories in Berlin undoubtedly did good work, mainly directed towards the making of large easily filterable crystals of the dihydrate type⁽³⁾.

The Anhydrite Process

When the means had been found for the precipitation of calcium sulphate as anhydrite crystals, further research work was performed with the object of establishing a technical process based on these facts. Considerable experience was gained by this work. Its results were protected by a series of patent applications in different countries of which the British one with application date September 8th, 1931 led to patent rights in 1932 (British patent 378,670). Inventor as in the cases mentioned before was Sven Nordengren, Landskrona⁽⁴⁾.

(2) See also Belgium 360.054, Denmark 41.198, France 672.846, Holland 37.793, Italy 279.675, U.S.A. 1.776.593, and others; followed by Belgium 360.055, Denmark 41.199, France 672.847, Italy 286.132, Switzerland 150.904, Spain 112.259, Sweden 69.706, and others.

(3) British patent 301.864 and 309.023.

(4) See also Belgium 390.476, Denmark 48.080, France 751.903, Holland 38.681, Canada 343.714, Switzerland 164.831, Sweden 91.261, Germany 716.217, U.S.A. 2.002.547 and others.

The patent specifications show that this work was and still is of fundamental importance in the principles employed in making phosphoric acid according to the anhydrite process. The theories of the process were explained and the border lines of temperature and concentration were established. Also the means of obtaining large, easily filterable crystals of anhydrite were described. It would be impossible to-day to make phosphoric acid according to the anhydrite process without coming into contact with the claims of the said patents. However, no patent rights based on the original applications are in force at the present time.

In British patent 378.670 the following was recorded (in 1931) : "Of importance are the three factors temperature, concentration and time. Of these the most important are temperature and the concentration, and the relation between these to obtain the desired stable form may be expressed by the equation $2p + t =$ at least 186, where "p" is the concentration of the phosphoric acid present at or after the reaction expressed as per cent. by weight of P_2O_5 in the mother liquor, and "t" is the temperature at the stabilization in degrees centigrade. In actual practice it may be preferable to use a somewhat higher temperature, e.g. 5 - 10°C higher."

This is in fact still the main rule of the anhydrite method. If, for instance, the mother liquor contains 43% P_2O_5 by weight, then the minimum temperature should be 100°C, and preferably increased to 105 - 110°C.

It was also known at that time, about 1930, that phosphoric acid either in filtered form or as part of the sludge should be circulated in the process. It was further found that the concentration of the mother liquor should be increased so that the necessary temperature could be reached beneath the boiling point which made it possible to perform the operation in open vessels. Other important facts can be found in the patent specifications.

Further Development of the Phosphoric Acid Processes

The detailed knowledge of how to produce strong phosphoric acid according to the anhydrite method would undoubtedly have found an industrial application at an earlier date, but for certain technical difficulties.

At the time when those investigations were performed no suitable filter was available for the separation of the calcium sulphate. Further, there was no filter cloth that could withstand strong phosphoric acid. After some time the rubber belt filter of G. Wallny, Landskrona⁽⁵⁾ was brought on the market. It was, however, best suited for acids up to 30% of P_2O_5 . The filtering process was simple. The mother liquor was drawn off, whereupon the filter cake was

(5) Sven Nordengren : The Horizontal Filter, Mining Magazine, July, 1949.

washed, first with a wash liquid containing 5-10% P_2O_5 , then with water. The limiting temperatures for making dihydrate crystals, $CaSO_4 \cdot 2H_2O$, had been established⁽⁶⁾. These temperatures also gave the best crystals at a concentration of the mother liquor of 30% of P_2O_5 , the optimum temperature was 80°C. A sludge containing 30% of P_2O_5 could be filtered on a Wallny fiber belt filter with wool cloth which had a working life of about a month.

Consequently, the dihydrate method came generally into use for acid of 30% P_2O_5 . The acid was concentrated further by the use of hot air or by oil burners.

There still existed, however, a demand for a process in which strong phosphoric acid could be manufactured in a direct way, also, if possible, with higher yield than the 94% usually obtained in the dihydrate process.

Several years ago a new filter for the chemical industry came into the market, the Nordengren Tray Belt Filter. By means of this filter it is possible to wash the sludge from the anhydrite process with 4-5 wash fractions. This number is necessary to keep up the concentration of the circulating phosphoric acid. At the same time plastic filter cloths were brought into the market. These permitted the filtration of 43-45% P_2O_5 acid at a temperature of 80-90°C.

It was now possible to realize the anhydrite process on a large scale. A plant according to this method with a capacity of 15 tons of P_2O_5 per 24 hours was planned and designed by Nordengren & Co., A.B., of Landskrona, Sweden. The plant was built by the Prodotti Chimici Superfosfati S/A, Vercelli, Italy, and put into production in the spring of 1953. It was found that in order to get good results certain modifications had to be made in the process of 1930. These modifications were all developed at Vercelli by the designers beforehand and from experience when the plant was being started up. They are certainly of original character and will consequently be protected by patent rights.

Design of the Vercelli Plant

The plant is built for a maximum capacity of 15 tons of P_2O_5 per 24 hours in the form of phosphoric acid of 40-45% P_2O_5 . The primary materials are sulphuric acid 75-82% H_2SO_4 and phosphate rock ground to a fineness of about 95% through screen DIN 40. Three types of phosphate rock have been used up to date: 34% P_2O_5 Khouribka (Morocco), 30% P_2O_5 M'Dilla and 27% P_2O_5 (low grade) Gafsa. Mixtures of these different grade rocks have also been used.

(6) Sven Nordengren: The Double Superphosphate and Wet Phosphoric Acid Processes, Acta Polytechnica, Stockholm 46/1949.

Fig. 1 is a diagram of the plant. This can be divided into two distinct parts. The feeding section together with the vessels for the precipitation of anhydrite forms one part and the filtering section where the sludge is washed comprises the second part.

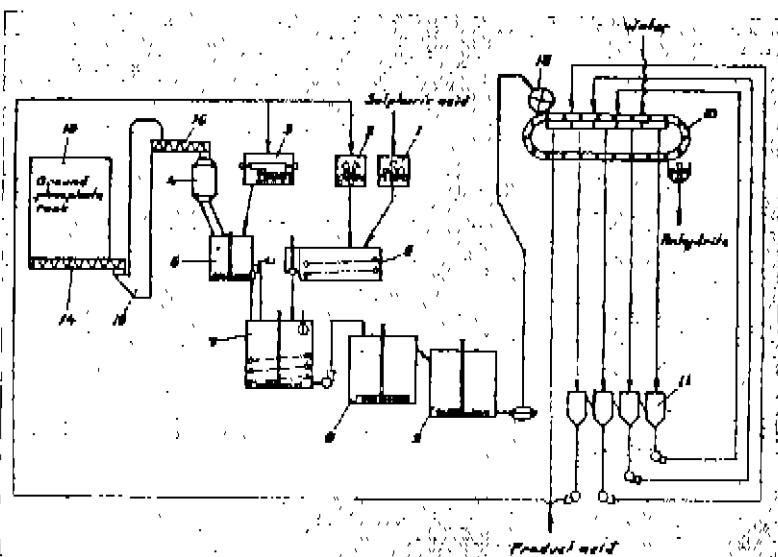


Fig. 1 — Flowsheet for the Phosphoric Acid Plant at Vercelli.

In the anhydrite process, the precipitation is carried out in such a way that the crystals will be formed as filterable anhydrite under controlled conditions. This is done by adding heat and by following a special sequence during the precipitation. Ground phosphate is taken from the silo 13 via the screw conveyor 14, elevator 15, and screw feeder 16 to the automatic weighing machine 4. The weigher is synchronized with the acid feeding buckets 1, 2 and 3. The acid feed buckets 1 and 2 for sulphuric acid and circulating phosphoric acid respectively are made in sheet lead in form of quadruple buckets for continuous feeding of a measured flow into the heating tank 5.

Phosphoric acid feed bucket 3 is a single lead lined bucket feeding acid to the mixer 6, which also receives ground phosphate rock in corresponding portions from the weigher. The phosphate rock and acid are agitated together for a short time forming a sludge of over-acidulated triple superphosphate, or predominantly mono-calcium phosphate with excess phosphoric acid. Each batch is then released into the reactor 7. The mixer is intermittently emptied by an automatically operated valve which is synchronized with the weigher. The phosphoric acid recirculated in the process, and the

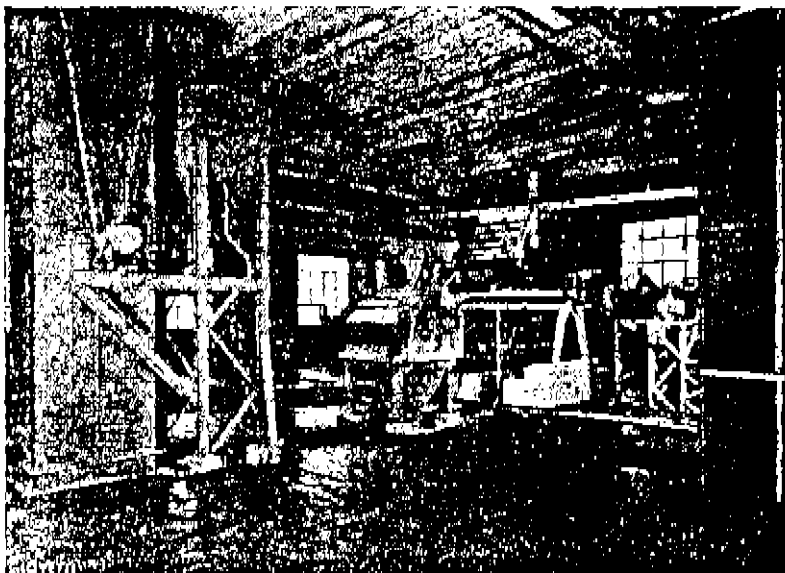


Fig. 2. — Ground phosphate weigher and acid feeders.

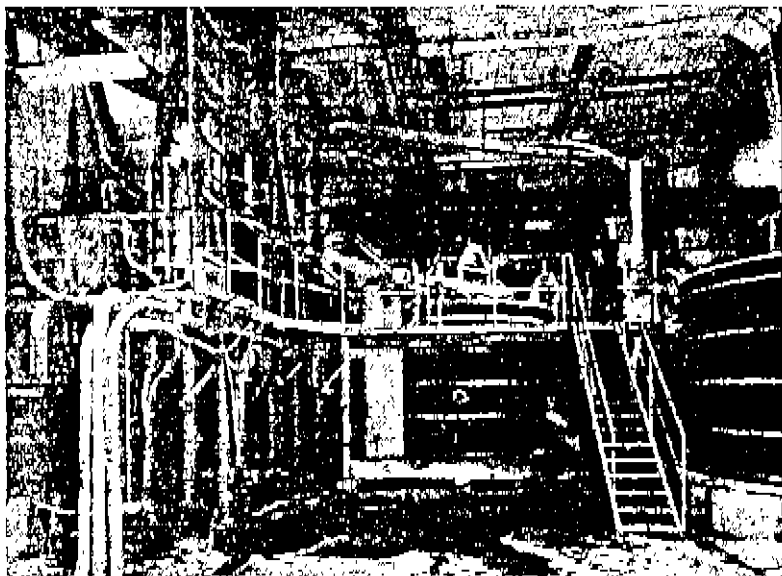


Fig. 3. — Phosphoric Acid Plant at Vercelli; view of ground floor.

sulphuric acid are fed into a heating vessel 5. In the heater the temperature of the mixed acids is raised to 135°C. The hot acids are released into the reactor 7 at regular time intervals. The heater is lead-lined and equipped with a heating coil. It is regulated by a special control system inter-connected with the weigher and a thermostat.

Dow-therm liquid, circulating through the heater 5, and the reactor 7, serves as a heating medium picking up heat from an economizer in the sulphuric acid plant, where waste heat from the cooling air of the pyrites burners is utilized.

The reactor is a lead-lined vessel, equipped with a slow-type stirring device and a mechanical froth disperser coupled to the stirrer shaft. Here the main reaction takes place and the anhydrite crystals are precipitated and agglomerated.

The after-reaction vessels or digesters 8 and 9, are similar to the reactor, but there is no heating coil and no anti-froth device. The

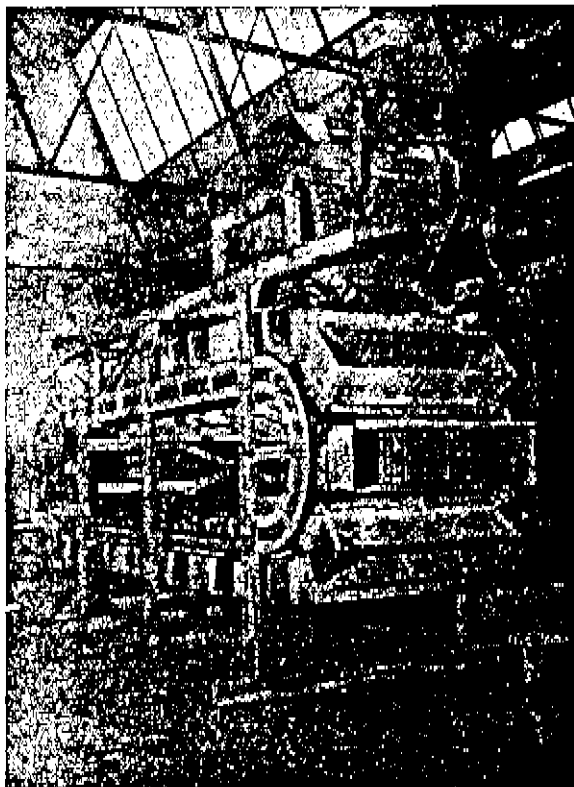


Fig. 4 - - The Nordengren Tray Belt Filter.

sludge formed in the reactor leaves the last digester which is equipped with means of cooling down to a temperature of about 80°C. The retention time is 3 to 4 hours,

The filtering section consists of a Nordengren Tray Belt Filter 10, barometric legs, hydraulic closures, circulation regulators for the wash liquids 11 and vacuum equipment for the filter. As was mentioned earlier, the invention of the Tray Belt Filter is one of the things which has made the evolution and the industrial practice of the anhydrite method possible. The filter consists of a series of pans or shallow trays travelling on a rack. The trays form an endless belt, and each tray in upright and horizontal position is in vacuum connection with a suction box, situated beneath the trays, by means of armoured rubber tubes, via a suction rope of rubber or other flexible material which slides over a narrow slit in the lid of the suction box. The filter is horizontal and can be built in big units. It can be made in acid proof material or lined with plastic or rubber to withstand attacks by corrosive agents. The trays and the horizontal lay-out make counter current washing in several steps possible. All parts of the filter are easily changeable but so far maintenance has proved to be small on the filters already installed. To ensure that the trays will all be filled up to the same controllable depth and thereby to regulate the thickness of the filter cake, the filter is equipped with a rotating feeder 12 which is synchronized with the movement of the trays. The feeder is constructed in such a way that the

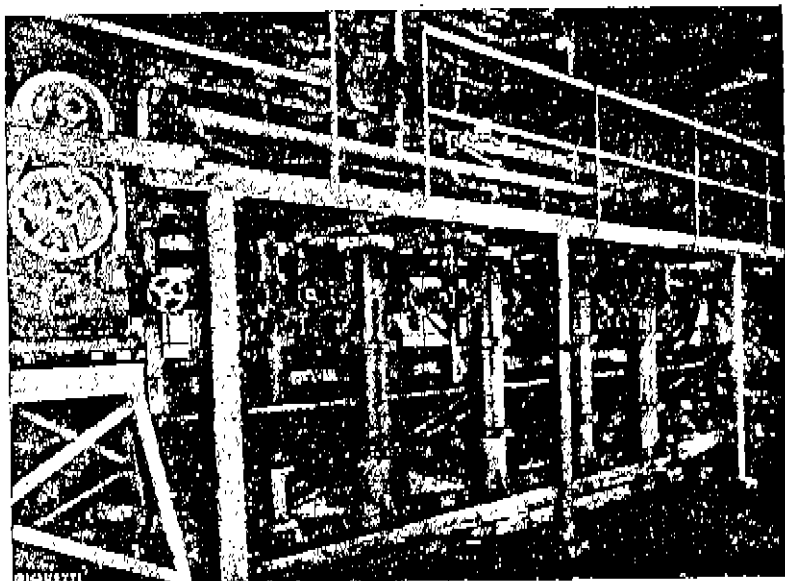


Fig. 5 — Filter and filtrate pipes.

filter cake thickness can be varied continuously from zero up to 6".

The filter is placed on barometric height to avoid difficulties with sealing which would occur in extraction pumps and to facilitate cleaning and operation of the plant. The filtrates are taken out in five discharge columns with liquid seals at the ground floor. The mother liquor in the first barometric leg has a strength of 42 - 45% of P_2O_5 . In the second barometric leg flows acid of about 40% P_2O_5 , which is to be recirculated in the process by dividing, part to be mixed with the sulphuric acid and heated and part to form the over-acidulated triple superphosphate or monocalcium phosphate sludge in the mixer. The three remaining filtrates contain 35, 20 and 5% P_2O_5 respectively. These three acid liquors are passed through the filter in turn, followed by water, thus forming a counter-

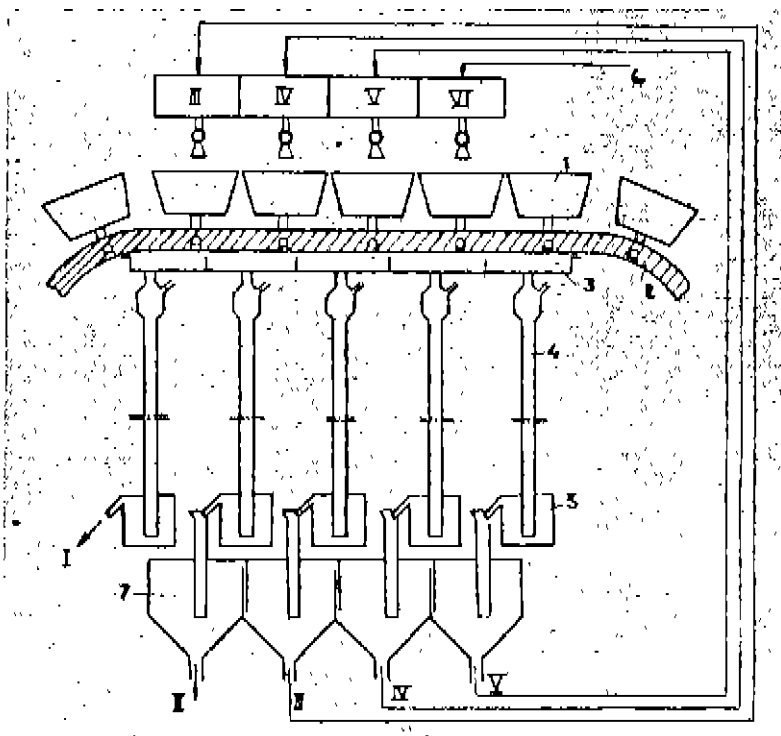


Fig. 6— Flowsheet for wash liquids.

I, Product : II, Circulating phosphoric acid : III, IV, and V, Wash liquids : VI, Water : (1) Tray Belt : (2) Suction belt : (3) Suction box : (4) Filtrate pipes : (5) Liquid trap : (6) Water pipe : (7) Receivers.

current wash system.

To regulate the flow of wash liquids on the filter in relation to the filtrates, the plant is equipped with a filtrate circulating regulator shown on fig. 6. This consists of a series of receivers which are connected with each other by means of overflow tubes. During normal work very little liquid will shift from one container to another, but if some irregularity should occur, acid will flow from the two adjacent containers into the one deficient of acid, and if a surplus of acid should be at hand it will flow to both sides, thus maintaining the relative concentration of wash acids in the system. The water is added at filter level and flows down after passing the filter cake as 5% P_2O_5 acid into the filtrate circulating regulator. From the end of the circulating regulator flows circulating acid which is transported back into the reaction. In this way wash water given on the filter passes the circulation regulator and the filter in counter

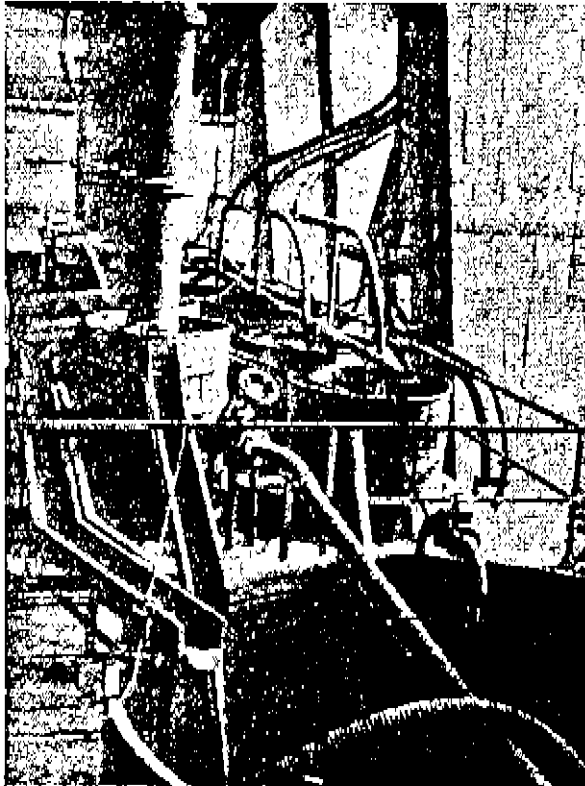


Fig. 7 - Circulation regulator for wash liquids.

current with the anhydrite, taking up P_2O_5 until it reaches the necessary strength for circulating acid. Product acid does not enter the regulator, but goes directly into the product tank through an overflow on the acid seal tank leading into the main tank for circulating acid.

Another cause of difficulty in the original anhydrite process during the early work was the absence of a filter cloth able to withstand hot, strong acids. The rapid evolution of the plastic field during and after the last war has led to a number of excellent fabrics which can withstand concentrated and relatively hot acids. Most of those used to-day in phosphoric plant are made of polyvinyl chloride base and are able to withstand a temperature of 80 - 90°C. At the present date fabrics exist which can take still higher temperatures without notable shrinking or deterioration. A long discussion has been held regarding the various advantages of the two general types of cloth, the monofilament cloth with high twisted yarn and the multifilament type.⁽⁷⁾ Our experience is that when filtering large single crystals both types could serve equally well, but if fragile agglomerates are to be filtered, the bridges built over the large apertures in the monofilament cloth can break down blinding the cloth. It is important, however, in both types that the absorption factor of water is very low, otherwise the acid will be diluted by water left in the cloth from the back wash. About ten different types of filter cloth were tried out during the starting up of the anhydrite plant at Vercelli. Best of these was the Belgian Lalnyl cloth of multifilament type which gave rapid filtration and had the advantage over other cloths in that it was almost immune to clogging. In fact we have had the same cloth on the filter for about seven months without need of replacement.

The Intermittent Reactor Process

It is always a large undertaking to develop a process which has been tried out on a laboratory or pilot plant scale into an industrial plant. There are things which cannot be foreseen and many difficulties which have to be solved on the drawing board and in the planning before the actual construction of the plant begins. We knew by the early investigations how to make relatively stable anhydrite crystals and we also obtained agglomerated crystals at that time. The problem was then that we did not know why the crystals mostly were agglomerated, and why under slightly changed conditions, we had a certain difficulty in obtaining parallel results. During the construction and trials of the plant at Vercelli we continued our experimental work and developed a new operating sequence for the precipitation, with the result that crystals can now

(7) Chem. Eng. Progr. Vol. 47, No. 11, p. 545.

be obtained in agglomerated form under completely controlled conditions. We know the temperature limits within which it is necessary to work and we have developed the simplest possible practice. The rather complicated apparatus which was necessary before these developments has been changed and simplified.

The precipitation takes place in a vessel which we call the anhydrite reactor. The anhydrite method is a continuous process but it is necessary to have the reactor intermittently charged in order to get the very high filtration speeds which allow the concentrated phosphoric acid to be washed out. A mixture of sulphuric and phosphoric acids in defined proportions is first fed into the reactor at a temperature of 135°C. Supersaturated triple superphosphate sludge which has been stirred for a short time is then added to the hot acid in portions, following a definite time schedule. The reactor is heated in order to keep the temperature under control during the precipitation. The difference between other processes in general where filterable sludge is to be obtained, e.g. the dihydrate process, is that in most processes crystals are made to grow to a size which enables them to be filtered off within an allotted time interval. This is not the fact in the anhydrite process. The crystals are agglomerated to obtain a filterable size.

The Building up of Crystals

In order to study what is happening when calcium sulphate is precipitated from the newly formed sol of monocalcium phosphate, it is useful to make a comparison with the behaviour of colloids. The theory of the stability of colloids is based on the supposition that the particles are electrically charged. This is a surface phenomenon which is caused by preferential adsorption of a positive or a negative ion from the substances which are present in the liquid. Particles with electric charge of the same sign repel each other and remain in suspension if the gravity field is low.

To precipitate a colloid it is necessary to destroy this electric balance by introducing another colloid, charged with the opposite sign, or to alter the ion concentration by adding an electrolyte. This is known as flocculating and is a very important process in the technological field. It is believed that the flocculation is caused by cohesion forces between the particles drawing them together into large aggregates which have a higher sedimentation speed.

The neutralization of the electrically charged particle is due to the fact that ions of the opposite sign are taken up in the surface layer of the particle. Sometimes this is purely an adsorption of new ions; at other times these ions may react chemically with the previously adsorbed ions. Further the increased 'ionic strength' obtained by adding the electrolyte can cause the counter charged ions in the solution surrounding the particle to be forced against the adsorbed

ions so that these are neutralized. The conventional size limit of particles in colloidal solutions is 0.1μ . It might be assumed that the behaviour of primary particles from a precipitation forming a true suspension, should be essentially the same, and this has in fact proved to be the case. Aggregation of primary particles is analogous to the flocculation of colloids and is likewise strongly dependent on the amount of ions in the solution. An increase in the 'ionic strength' gives an increase in size of the agglomerates.

The equipment to bring about flocculation on a technical scale is normally very simple. The electrolyte which is to act as flocculating agent is added and very intimately mixed with the suspension. The probability of each particle coming within attraction range is increased by having a slow agitation in the vessel in which the agglomeration is taking place. There needs to be a slow movement within the system, but care must be taken not to agitate the flocculating sludge too strongly, submitting the agglomerates to mechanical stress. They are very fragile and can easily be broken up, being held together by minute forces.

The foregoing practice was taken up by us in the anhydrite process. The stirring in the reactor is adjusted to the optimum figure without breaking up the nuclei. By using a large excess of acids in the initial phase of the precipitation, the 'ionic strength' is kept high so that agglomerates are formed. When the precipitation gets near completion the temperature falls and the 'ionic strength' decreases. By then there are already so many large agglomerates and very few small nuclei that crystals still being formed under the progressively less favourable conditions build on to existing agglomerates. These, in turn tend to undergo further agglomeration and to join together in long chains, a phenomenon which might explain the unusually high filtration speeds which can be reached with this method. This can be seen clearly in fig. 8 which shows phosphoric acid sludge not subjected to mechanical handling. Fig. 9 shows a single agglomerate considerably enlarged. The nucleus can be seen and also the growth of crystals on the outside of the nucleus where the typical short anhydrite crystals are hanging in a cluster. Fig. 10 shows anhydrite which has been washed on the filter. The crystals look completely stable and no recrystallization has taken place. The long chains shown on fig. 8 have, however, broken up, and the individual agglomerates are single. They are rather large and uniform in size and the amount of individual small crystals is low which enables them to pack into a very loose filter bed. However, owing to the slight forces which keep the crystals together in agglomerates, they are very sensitive to mechanical handling. For transport of the sludge, membrane or plunger pumps must be used which do not subject the material to undue stress. It cannot be pumped with a centrifugal pump without breaking up the agglomerates to a certain extent. The passage through a centrifugal



Fig. 8 -- Agglomerated anhydrite crystals: sample from acid sludge.

Fig. 9 -- A single anhydrite agglomerate in large magnification.

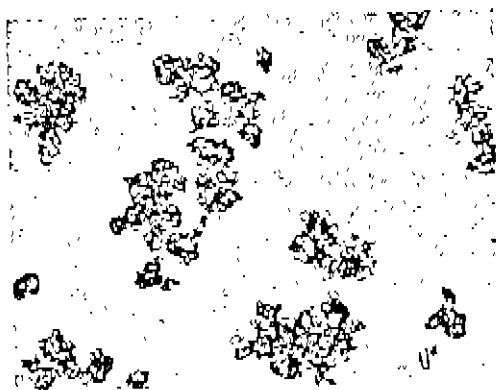


Fig. 10 -- Anhydrite sample taken after the soluble P_2O_5 has been washed out with water on the filter.

Fig. 11 -- Sample from plant deposit: age about 2 years. The crystals are slowly recrystallizing into dihydrate.



pump will reduce the filtrability of the sludge by about 50%. This is a high figure, but at the Vercelli plant the sludge is transported from the reactor to the after-reaction vessel by means of a centrifugal pump, and still it retains a filtration speed which is higher than the average filtration speed in a dihydrate plant.

Another point of interest is that surface active agents used, for instance, against froth, must not be utilized in this process as they immediately break up the agglomerates and reduce the filtration speed of the sludge to about 10% of what it was before. This has been one of the difficulties which we have had at the Vercelli plant. Several times at the beginning it happened that a tube in the heating coils broke and the dow-therm liquid entered into the sludge or acids. Dow-therm is diphenyl oxide in admixture with diphenyl, is surface active, and when it entered into the sludge the filtrability decreased sharply.

The anhydrite crystals formed in this process are not completely stable. Fig. 11 shows anhydrite which had been lying on the waste deposit for two years. It can clearly be seen that this sample has recrystallized. At the left in the figure is shown a big cluster of anhydrite crystals just recrystallizing into dihydrate. On the right hand side is a big dihydrate crystal. The recrystallization of anhydrite to gypsum is, however, of no consequence to the filtering. It is only important that the recrystallization should not take place on the filter so that the washing is hindered. Owing to the varying temperature range within which we are able to work we can control the time of this recrystallization from one hour after the filtering up to several months or even a year after filtration, the whole while in contact with water.

Starting up of the Anhydrite Plant

In the anhydrite process part of the acid from the filter is taken back to the feeding section and recirculated. When this plant was going to be started up there was no phosphoric acid available and the plant had to be started up on water instead of circulating acid. This meant that the plant had to operate in the zone of the concentration/temperature diagram fig. 12 where the calcium sulphate crystallizes in an unstable form. If, however, the reaction is carried out in a certain way it is possible to get the crystals stable for a certain time interval. This time is longer the nearer the borderline for stable crystals one is operating, but it is only necessary for this time to be long enough for the filtration to be finished before the gypsum cake hardens.

A mixture of water and sulphuric acid was charged into the reactor. The diluted acid was heated to just below the boiling point. Ground phosphate and water were charged into the mixer and let out in portions during a certain time. During the feeding, heat was

added in the reactor and the sludge was allowed to reach the boiling point for one hour after the conclusion of the feeding. The boiling point of the sludge was at completion of the feeding 103°C . but the temperature during the reaction was kept one or two degrees below the decreasing boiling point. When the sludge had cooled down to about 80°C a filtration sample was taken. About 50% of the crystals were anhydrite, the rest non-stable hemi-hydrate and dihydrate. The cake took about one hour to harden and the filtering speed was more than sufficient. The hydraulic closures and the circulating regulators were filled with water and the sludge was filtered off. This procedure was repeated in batches and as a result phosphoric acid with about 9% of P_2O_5 was obtained. The mother liquor contained 20% of P_2O_5 , but was diluted with the water initially used in various sections of the plant.

The weak phosphoric acid produced was used as circulating acid and the concentration of this was slowly increased until normal working conditions were obtained with a product acid of 45% P_2O_5 and the correct amount and concentration of the circulating acid. The concentration of the mother liquor for each operation may be seen in fig. 12 by following the direction of the arrow. As the concentration increased by working in this way, the amount of circulating acid had to be increased successively in order not to

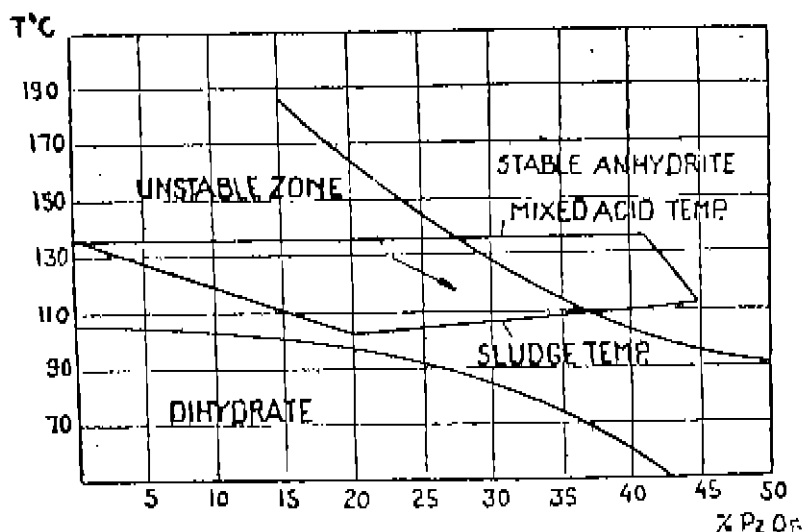


Fig. 12 — Diagram of temperatures and concentrations. The quadrangle shows reaction temperatures and concentrations during the starting up of the Vercelli Plant.

block the mixer. During this concentration period acids of various strength were produced. All acids were taken back in the process until the product had reached a concentration of 30% P_2O_5 . Then this acid was used for enrichment of superphosphates. A halt in the increase of concentration was called at 30% P_2O_5 , partly to try out a suitable filter cloth, partly to train the personnel. Whilst working in the non-stable zone only a part of the crystals precipitated as anhydrite. A certain amount of dihydrate and hemi-hydrate crystals got into the filter cloth, blinding it severely. It was during this period that the Lainyl cloth proved its superiority. When 45% P_2O_5 product acid was obtained a number of trials were made in order to get the highest efficiency in the machinery and the simplest operation of the plant. These tests resulted in what we now call the intermittent reactor process, described above.

Normal Working

Some interesting experience has been acquired during the time in which the plant has been working, some of which has already been mentioned. We would like to add something about cleaning and corrosion, two of the biggest problems in a phosphoric acid plant. Cleaning work has proved to be considerably less annoying than when operating a dihydrate process plant.

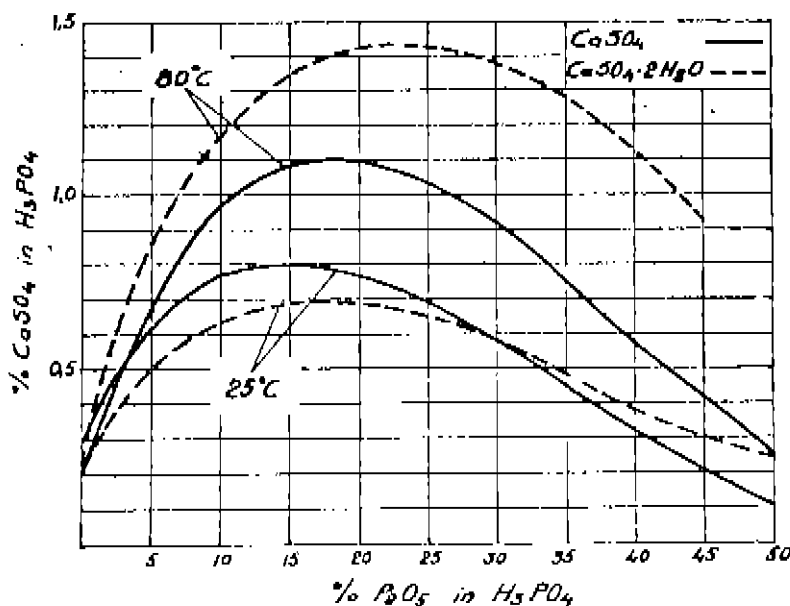


Fig. 13 — The solubility of anhydrite and gypsum in phosphoric acid at 25° and 80°C.

The solubility of calcium sulphate in its different crystal forms (fig. 13) is much higher for dihydrate nominally being worked at 30% P_2O_5 concentration than for anhydrite worked with an acid concentration above 40% P_2O_5 ⁽⁸⁾. Further, the difference between the solubility at 80°C and 25°C is much less for anhydrite than for gypsum at their respective working concentrations. Even allowing for the tendency of calcium sulphate to form supersaturated solutions in phosphoric acid, this is very important because when acids are cooled calcium sulphate will precipitate and give rise either to loose calcium sulphate deposits or to scaling.

The extremely hard scales formed by fluorine together with the gypsum on many points in a dihydrate plant, which are difficult from the cleaning point of view, are not nearly so prevalent in an anhydrite plant since the high temperature in the acid heater and during the main part of the reaction, drives off the greater part of the fluorine. Analyses have shown that the fluorine content in the product acid from the Vercelli plant lies around 0.3 - 0.5% F, against the dihydrate process figure of about 1.5% F. This not only gives the acid better quality, but it also diminishes the scaling and so the cleaning in the plant itself. The loose deposits of calcium sulphate should naturally also be less in an anhydrite plant, a fact which has been confirmed by working experience at Vercelli.

The construction materials used in contact with hot strong phosphoric acid are lead, rubber and stainless steel 18/8/2.5. The stainless steel has proved its value in pumps and other equipment, but does not stand up to the demands at the points of high temperatures. Lead has shown very good properties, and the lead in the tanks, heater and reactor has not been visibly changed by corrosion. It happened, however, sometimes that the heating coil for dow-therm had a break-down but this was probably due to the continuous expansion and contraction of the heating tubes when starting and stopping the plant. Later the acid heater was modified, the coils being made in shorter units working in parallel, since when the difficulty has disappeared. Lead used in other parts of the plant has not been affected at all.

All tubing for phosphoric acid and all valves are rubber and rubber-lined respectively. Rubber has stood up very well to acids up to 90°C which is the maximum temperature to which it has been subjected. The reason why we have chosen rubber tubes rather than lead, is that they can be cleaned more easily.

Heat Consumption

The heat which has to be supplied to the Vercelli plant costs nothing as the waste heat from the cooling air from the pyrites

(8) J. Appl. Chem. U.S.S.R., 18, 1945, p. 521.

burners of the sulphuric acid plant can be used. By measuring quantities and temperatures the amount of heat utilized at present has been calculated to be about 450,000 k. cal./ton P_2O_5 produced.

A cautious calculation shows that by effective lagging of tubing and receivers for the circulating acid as well as of the vessels where the reaction takes place, this figure could appreciably be diminished and that the savings in fuel compared to the evaporation of dihydrate process acid to 45% P_2O_5 would amount to about 60%. If contact acid were available, the dilution heat should theoretically make external heating unnecessary, and the plant could be self-supporting, granted that the rate of throughput was great enough in proportion to the heat losses through radiation and convection.

Results

A new method of making strong phosphoric acid has been tried out in a full size plant. The concentration is high enough to permit the acid to be used for the manufacture of concentrated superphosphate without previous evaporation.

The high temperature of the reaction makes the yield high and the attack swift. The yield of attack naturally depends on the time of reaction. After about 3 hours an attack yield of 97 - 98% has been reached when Morocco phosphate was used.

The results of filtration have shown that about 98% of the water soluble P_2O_5 can be washed out of the sludge on a tray belt filter with a concentration of the first filtrate of 43 - 45% of P_2O_5 . The residual 2% is naturally in solution in the moisture of the cake, calculated to be about 40% of the dry weight of the cake. Centrifuging of the cake may extract about $\frac{2}{3}$ of this moisture with its P_2O_5 content which can then be returned to the process. This would make the total yield exceeding 97% a figure which cannot be reached in the dihydrate process. The very high filtering speed attained by the intermittent reactor process makes the filter area small and the filter relatively cheap.

Also, the short time of reaction makes the digesters small. The space taken up by an anhydrite plant will only be about half of the space required by a dihydrate plant with the same output of P_2O_5 . The building and machinery costs will be in proportion.

A phosphoric acid plant contains two parts, the section for the attack, and the filtration section. The first can be wholly mechanized so that it can be started or shut down by pressing a button. The filters should be watched very carefully by especially trained personnel, but as they can be made in any size, larger plants do not need more supervision than smaller ones. The anhydrite process is on the whole, especially suitable for large plants.

It is believed that as a method has now been found which permits of the production of large quantities of strong phosphoric acid without any great cost or loss of phosphorus, and as the costs of plants for this method are comparatively low, the main phosphorus containing fertiliser will no longer be ordinary low-grade superphosphate, but products in which the phosphorus has passed the phosphoric acid stage. Undoubtedly the general tendency in fertiliser manufacture is towards high-grade granular compounds. The future production of such fertilisers will demand large quantities of phosphoric acid.