

ISMA* Technical Meetings

Paris, France

25-27 September 1951

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

LE/271

90 (1951)

661.634

ACTA POLYTECHNICA

Part No. 9

CHEMISTRY INCLUDING METALLURGY SERIES Vol. 2 Nr 9

SVEN NORDENGREN:

**Studies on the Production of strong Phosphoric Acid
according to the Wet Anhydrite Process**

ACTA POLYTECHNICA is devoted to original contributions to engineering sciences and is published at Stockholm, Sweden, by the Royal Swedish Academy of Engineering Sciences in collaboration with the State Council of Technical Research, The Royal Institute of Technology, The Chalmers' University of Technology (Gothenburg), The Association of Engineers and Architects, and other bodies.

Also published as **INGENIÖRSVETENSKAPSAKADEMIENS HANDLINGAR Nr 206**

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STUDIES ON THE PRODUCTION OF
STRONG PHOSPHORIC ACID ACCORD-
ING TO THE WET ANHYDRITE
PROCESS

BY

SVEN NORDENGREN



INGENIÖRSVETENSKAPSAKADEMIENS

HANDLINGAR NR 206

1951

GENERALSTABENS LITOGRAFISKA ANBTALTS FÖRLAG
STOCKHOLM

RECEIVED BY THE ROYAL SWEDISH ACADEMY
OF ENGINEERING SCIENCES IN FEBRUARY, 1951

Engelska skriftbolaget
Stockholm 1951
101000

Studies on the Production of strong Phosphoric Acid according to the Wet Anhydrite Process

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661.634

As previously shown by the author, the calcium sulphate, constituted when ground phosphate rock is disrupted by sulphuric acid, can be formed either as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, dihydrate, as $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, hemihydrate, or as CaSO_4 , anhydrite.¹ All these forms of calcium sulphate can be obtained as large, stable, easily filterable crystals or as stable, easily filterable agglomerates of smaller crystals. The crystal forms depend on the temperature and concentration of the mother liquor. When the crystal water tension is lower than the vapour tension of the mother liquor, crystals with crystal water are formed and vice versa. A lower temperature and a lower concentration of the mother liquor gives a higher content of crystal water. At the present time phosphoric acid, produced according to the wet process, is received in a concentration of about 30 % P_2O_5 ; the temperature in the digesters should not be raised to more than about 80° C, and easily filterable crystals are formed as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. At a higher temperature, part of the CaSO_4 will form unstable $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ or even CaSO_4 , and the cake will harden on the filter, as these unstable forms will take up crystal water, making the cake impenetrable to the wash liquids.

The best way to make stable hemihydrate crystals, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is to perform the disruption in an autoclave. The mother liquor should contain about 30 % P_2O_5 . The sulphuric acid and the circulating phosphoric acid are preheated so that a temperature of about 135° C is reached in the autoclave. This process gives the highest yield of all, more than 99 %.

In both these processes, a phosphoric acid is obtained with about 30 % P_2O_5 , and this acid has to be concentrated to 45–50 % P_2O_5 before it can be used for the production of concentrated superphosphates. It has now been found that it is possible to reach a concentration of 45 % P_2O_5 in the mother liquor. The calcium sulphate will then be formed as anhydrite, CaSO_4 .

To reach the said concentration, to get a comparatively good yield and to receive, at the same time, stable anhydrite crystals is comparatively easy. It is, however, difficult to form good-sized anhydrite crystals and at the same time to obtain an easily filterable sludge. The conditions necessary for this purpose have been studied by the author and the results will be given below.

1) S. NORDENGREN: The Double Superphosphate and Wet Phosphoric Acid Processes: their present State and future Possibilities, IVA:6 Handling Nr 203, Stockholm 1949, and Acta Polytechnica Nr 46, Stockholm 1949.

General Remarks Regarding the Trials

All trials were made on Morocco Phosphate with about 34 % P_2O_5 . The phosphate was, as a rule, ground to the same fineness as for superphosphate production, or about 85 % through DIN 40 (practically 100 mesh). It is believed that a finer grinding will give a higher yield.

The sulphuric acid used was Glover acid from a lead chamber plant, diluted to 75 % H_2SO_4 . The quantity was 0.89 parts of 100 % H_2SO_4 to 1 part of phosphate.

In all trials a quantity of strong phosphoric acid was added, usually containing 45 % P_2O_5 . In trials Nos 57—63 the concentration was lowered to 43 % P_2O_5 , which greatly improved the filtration speed. The quantity of phosphoric acid thus returned to the process was measured in the following way: its content of P_2O_5 was calculated as a certain multiple of the content of P_2O_5 in the ground phosphate. This "phosphoric acid factor" varied between $f = 3$ and $f = 5$. When, for instance, $f = 3$, the quantity of P_2O_5 returned to the process as strong phosphoric acid was 3 times the quantity of P_2O_5 in the phosphate.

In all cases, except in trials Nos 66 and 83—86, phosphoric acid was added to the ground phosphate in such a quantity as to form triple superphosphate, the quantity necessary being $f = 2.4-2.6$. In most cases a surplus was used. In trials Nos 29—86 phosphoric acid was also added to the sulphuric acid before the final reaction took place, the factor varying from $f = 0.9$ to $f = 2.7$.

A sample of the sludge was filtered on a horizontal laboratory filter with a filter cloth of wool. The filter had a surface of 0.045 square metres. The vacuum was kept at 35—40 cm Hg. The quantity of sludge was measured so as to give a cake with a thickness of about 60 mm. The wash liquids were 4 in number, with a P_2O_5 -content of 35, 20, 5 and 0 %. It should be noticed that the washing of the cake can be improved, so that practically no phosphoric acid is left in the cake. For the purpose of determining the yield and the speed of filtration the washing was, however, sufficient.

The filter cake was dried and analysed on total phosphoric acid — a % P_2O_5 and on water soluble phosphoric acid — b % P_2O_5 . The weight of the dried cake was determined to be 1.3 of the weight of the phosphate. If the content of P_2O_5 in the phosphate was c %, the yield was

$$x = 100 \left[1 - \frac{1.3}{c} (a - b) \right] \%$$

The content of P_2O_5 in the different filtrates was determined and, in some cases, also the surplus quantity of H_2SO_4 .

The filtering speed was measured for all filtrates. As the quantity of mother liquor varied with the quantity of phosphoric acid returned to the process (f), a calculation was made for each trial to determine the active surface necessary for filtering a production of 40 metric tons of P_2O_5 per 24 hours on a horizontal filter, for instance a Tray Belt Filter. It should be remembered that, if the washing out of the cake should be more complete, this surface should be increased with about 10 %. The figures are, however, commensurable.

All trials were made in the following way. A quantity of 2,400 g Morocco phosphate was mixed with a varying quantity of phosphoric acid. As a rule the temperature of this

phosphoric acid was the same as the temperature in the laboratory. The temperature was kept low in order to lessen the froth. At the same time 2,840 g of sulphuric acid with 75 % H_2SO_4 was heated in an isolated vessel with a diameter of 250 mm and a height of 450 mm. This quantity of sulphuric acid corresponds to 0.89 parts of 100 % H_2SO_4 per 1 part of Morocco phosphate. Sometimes this sulphuric acid was mixed with phosphoric acid. The vessel was lined with lead and had a lead-lined stirrer, rotating 130 r/min, the peripheral speed being 1.35 m/second.

The product obtained when the phosphate was mixed with the phosphoric acid, which mainly contained triple superphosphate, was left for 10—15 minutes and afterwards added in portions to the heated sulphuric acid or to the heated mixture of sulphuric acid and phosphoric acid. It was found to be essential to the process that the said product should be added to the sulphuric acid and not vice versa. In trials 1—2, 5—22, 25—35 and 39—86, about 10 % of the sludge from a previous trial was added to the sulphuric acid, or to the mixture of sulphuric acid and phosphoric acid, before the phosphate-phosphoric acid mixture was added.

The reaction time was 4 hours.

The trials can be grouped in the following way:

A. A fluent or semi-fluent mixture of phosphate and phosphoric acid was added to sulphuric acid or to a mixture of sulphuric acid and phosphoric acid

Table 1.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | Min. temp. of sludge °C | Thickness of cake mm | Filtering speed m ² /h | Filter surface for production of 40 tons P_2O_5 , 24h m ² | Dry cakes | | Yield % | Mother liquor % P_2O_5 |
|---------------|----------------------------|-----------------|-------|---------------------|--------------------|--------------------------------|-------------------------|----------------------|-----------------------------------|--|-----------------|-----------------------|---------|--------------------------|
| | mixed with | | total | Phos-phoric acid °C | Sul-phuric acid °C | Sludge during main reaction °C | | | | | tot. P_2O_5 % | water sol. P_2O_5 % | | |
| | Phos-phate | Sul-phuric acid | | | | | | | | | | | | |
| 1 | 3 | — | 3 | 20 | 125 | 100 | 85 | 60 | 3,500 | — | 0.70 | 0.09 | 97.7 | 45.85 |
| 2 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 5,300 | — | 0.60 | 0.04 | 97.9 | 41.36 |
| 3 | 3.5 | — | 3.5 | 20 | 120 | 100 | 80 | 60 | 2,100 | — | 1.39 | 0.70 | 97.4 | — |
| 4 | 3.5 | — | 3.5 | 20 | 120 | 100 | 80 | 60 | 2,300 | — | 3.88 | 3.77 | 95.8 | 45.56 |
| 5 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 6,300 | — | 0.87 | 0.05 | 96.9 | 45.02 |
| 6 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 3,000 | 11.5 | 1.32 | 0.67 | 96.7 | 46.26 |
| 7 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 2,300 | 14.8 | 2.49 | 1.16 | 94.9 | 43.34 |
| 8 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 920 | 38.4 | 1.34 | 0.47 | 96.4 | 56.75 |
| 9 | 3 | — | 3 | 20 | 120 | 100 | 80 | 70 | 1,800 | 13.9 | 1.19 | 0.31 | 96.6 | 48.18 |
| 10 | 3 | — | 3 | 20 | 120 | 100 | 80 | 65 | 5,600 | 7.1 | 1.11 | 0.24 | 96.6 | 45.14 |
| 11 | 3 | — | 3 | 20 | 124 | 100 | 81 | 60 | 1,900 | 18.7 | 0.44 | 0.32 | 97.6 | 45.00 |
| 12 | 3 | — | 3 | 20 | 120 | 100 | 80 | 60 | 2,800 | 13.9 | 1.81 | 0.28 | 94.1 | 46.51 |
| 13 | 3 | — | 3 | 20 | 120 | 100 | 78 | 60 | 2,500 | 15.7 | 1.10 | 0.35 | 97.1 | 48.24 |
| 14 | 3 | — | 3 | 20 | 124 | 100 | 81 | 60 | 1,400 | 17.1 | 0.87 | 0.14 | 97.2 | 48.28 |

At these trials, the whole quantity of circulating phosphoric acid was mixed with half the quantity of phosphate, the phosphoric acid factor being $f = 3$ to 3.5. This mixture was stirred by hand for about 10 minutes, after which time it became thick and semi-fluent. It was now poured down into the sulphuric acid which was heated to 120—125° C. Owing to its semi-fluent properties this part of the process took about 1 minute. After ½ hour the rest of the phosphate was added.

Sludge with a temperature of about 20° C from a former operation had first been added to the sulphuric acid, except in trials 3 and 4, which trials show a lessened filtering speed. When the sludge was added, the temperature sank from about 120° C to about 105° C. When the monocalcium sludge was added, the temperature was further lowered to about 80° C. Heat was added so that the temperature during the reaction was 100° C.

When the phosphate was added to the phosphoric acid, a considerable quantity of froth was formed. The volume of this froth was about twice the volume of the acid. When the monocalcium sludge was added to the sulphuric acid more froth was formed, also when the rest of the phosphate was added to the sludge. An addition of a small quantity of oleine had a favourable effect. Such addition had no influence on the forming of the crystals.

With regard to the filtering speed, the results are uneven, and although it is quite clear that a high concentration of the mother liquor will greatly lessen this speed (see trial Nr 8), there are other results which cannot be explained in this way. It was believed that the trials had been performed under conditions where a small change of either concentration, temperature or quantity of circulating phosphoric acid had a great influence.

Table 2.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | Min. temp. of sludge °C | Thick-ness of cake mm | Filtering speed m ² h | Filter surface for production of 40 tons P ₂ O ₅ /24h m ² | Dry cake | | Yield % | Mother liquor % P ₂ O ₅ |
|---------------|----------------------------|-----------------|-------|---------------------|--------------------|--------------------------------|-------------------------|-----------------------|----------------------------------|--|--------------------------------------|--|---------|---|
| | mixed with | | total | Phos-phoric acid °C | Sul-phuric acid °C | Sludge during main reaction °C | | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | Phos-phate | Sul-phuric acid | | | | | | | | | | | | |
| 15 | 3 | — | 3 | 20 | 135 | — | 80 | 50 | 1,150 | 35.0 | 1.34 | 0.34 | 96.0 | 46.40 |
| 16 | 3 | — | 3 | 20 | 125 | — | 85 | 50 | 1,250 | 31.0 | 0.90 | 0.17 | 97.0 | 48.40 |
| 17 | 3 | — | 3 | 20 | 133 | — | 91 | 50 | 2,500 | 14.1 | 1.05 | 0.33 | 97.3 | 39.50 |
| 18 | 3 | — | 3 | 20 | 135 | — | 92 | 50 | 2,100 | 16.5 | 1.48 | 0.51 | 97.4 | 47.44 |
| 19 | 3 | — | 3 | 20 | 130 | 100 | 90 | 50 | 1,500 | 19.8 | 1.12 | 0.39 | 97.3 | 42.73 |
| 20 | 3 | — | 3 | 20 | 130 | 100 | 85 | 50 | 1,200 | 31.0 | 0.96 | 0.38 | 97.3 | 42.72 |
| 21 | 3 | — | 3 | 20 | 135 | 100 | 90 | 60 | 1,200 | 26.0 | 0.98 | 0.36 | 97.6 | 45.34 |
| 22 | 3 | — | 3 | 20 | 122 | 100 | 90 | 60 | 2,500 | 13.2 | 1.34 | 0.63 | 97.5 | 45.53 |
| 23 | 3.5 | — | 3.5 | 20 | 125 | 100 | 91 | 58 | 2,300 | 15.8 | 0.96 | 0.17 | 97.0 | 45.46 |
| 24 | 3.5 | — | 3.5 | 30 | 130 | 100 | 85 | 60 | 3,000 | 12.8 | 1.08 | 0.30 | 97.3 | 44.15 |
| 25 | 3.5 | — | 3.5 | 20 | 122 | 100 | 81 | 60 | 2,000 | 18.5 | 0.72 | 0.10 | 97.7 | 42.55 |
| 26 | 3.5 | — | 3.5 | 20 | 125 | 100 | 80 | 60 | 2,800 | 13.0 | 0.85 | 0.19 | 97.3 | 44.43 |
| 27 | 3 | — | 3 | 20 | 133 | 100 | 88 | 60 | 1,700 | 21.6 | 0.72 | 0.19 | 98.0 | 43.08 |
| 28 | 3 | — | 3 | 20 | 120 | 100 | 82 | 60 | 1,900 | 18.2 | 1.10 | 0.32 | 97.1 | 44.01 |

During these trials, the circulating acid was kept at $f = 3 - 3.5$ and the whole quantity was mixed with half the amount of phosphate as in trials Nrs 1—14. During the trials 15—18 no heat was added during the first 80 minutes, and the temperature of the sludge dropped to about 15° C. The temperature was now raised to 110° C and was kept at this height during 80 minutes. During the last 80 minutes the temperature was allowed to drop to 85—91° C. During the trials Nrs 21—23 the temperature was kept at 90° C during 80 minutes, then 110° C during 80 minutes, and 100° C during the remaining 80 minutes, each 80 minute period representing the time of the sludge in one digester. It is quite clear that the temperature in the digesters, if high enough during a time sufficient to allow the forming of stable anhydrite crystals, has no dominating influence on the filtering speed.

The filtering speed is still uneven, but seems to be improved if the quantity of circulating phosphoric acid is increased from $f = 3$ to $f = 3.5$ (trials Nrs 23—26).

Table 3.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | | Min. temp. of sludge °C | Thickness of cake mm | Filtering speed m ² /h | Filter surface for production of 40 tons P ₂ O ₅ /24h m ² | Dry cakes | | Yield % | Mother liquor % P ₂ O ₅ |
|---------------|--------------------------------|----------------|-------|--------------------|----------------|------------------------------|--------------------------------|-------------------------|----------------------|-----------------------------------|--|--------------------------------------|--|-------------|---|
| | mixed with | | total | Phosphoric acid °C | mixed acids °C | Monocalc. sulphate sludge °C | Sludge during main reaction °C | | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | Phosphate | Sulphuric acid | | | | | | | | | | | | | |
| 29 | 3 | 1 | 4 | 20 | 137 | — | 100 | 113 | — | 1,600 | — | 0.93 | 0.20 | 97.4 | 43.49 |
| 30 | 3 | 1 | 4 | 20 | 115 | — | 110 | 110 | 50 | 4,700 | 9.0 | 1.22 | 0.20 | 96.2 | 50.20 |
| 31 | 3 | 1 | 4 | 20 | 135 | — | 110 | 105 | 50 | 4,500 | 10.0 | 0.60 | 0.14 | 98.2 | 46.22 |
| 32 | 3 | 1.4 | 4.4 | 20 | 132 | — | 110 | 103 | 50 | 2,000 | 20.0 | 0.87 | 0.16 | 97.3 | 46.12 |
| 33 | 3 | 1.4 | 4.4 | 20 | 138 | — | 110 | 107 | 50 | 2,200 | 16.6 | 0.83 | 0.16 | 97.3 | 44.07 |
| 34 | 3 | 1.4 | 4.4 | 20 | 135 | — | 110 | 105 | 50 | 3,400 | 11.5 | 0.53 | 0.05 | 98.0 | 47.45 |
| 35 | 3 | 1.4 | 4.4 | 20 | 135 | — | 110 | 106 | 50 | 3,100 | 12.0 | 1.01 | 0.27 | 97.2 | 49.66 |
| 36 | 2.7 | 1.3 | 4 | 20 | 137 | — | 110 | 105 | 55 | 3,600 | 9.5 | 1.26 | 0.19 | 95.2 | 48.12 |
| 37 | 2.7 | 1.3 | 4 | 20 | 135 | — | 110 | 110 | 55 | 2,700 | 12.0 | 1.01 | 0.24 | 97.1 | 46.55 |
| 38 | 2.7 | 1.3 | 4 | 20 | 135 | — | 110 | 110 | 60 | 3,000 | 11.0 | 0.91 | 0.20 | 97.3 | 43.27 |
| 39 | 3 | 1 | 4 | 20 | 135 | — | 110 | — | 65 | 4,000 | — | 0.86 | 0.05 | 96.8 | — |
| 40 | 3 | 1 | 4 | 20 | 135 | 25 | 105 | 98 | 70 | 3,200 | 11.0 | 0.87 | 0.04 | 96.8 | 43.67 |
| 41 | 3 | 1 | 4 | 20 | 135 | — | 110 | 105 | 65 | 2,700 | 13.0 | 1.25 | 0.28 | 96.5 | 45.60 |
| 42 | 3 | 1 | 4 | 5 | 135 | 15 | — | — | — | — | No filtration | — | — | — | — |
| 43 | 3 | 1 | 4 | 60 | 130 | 70 | — | — | — | — | — | — | — | — | — |
| 44 | 3 | 1 | 4 | 20 | 150 | 25 | 110 | 95 | — | 1,100 | 27.8 | 1.16 | 0.27 | 96.6 | 47.63 |
| 45 | 3 | 1 | 4 | 55 | 137 | 62 | 110 | 100 | 65 | 1,400 | 25.7 | 0.99 | 0.16 | 96.8 | 48.30 |
| 46 | 3 | 1 | 4 | 65 | 135 | 70 | 110 | 100 | 60 | 1,300 | 26.5 | 1.41 | 0.64 | 97.1 | 49.40 |
| 47 | 3 | 1 | 4 | 68 | 135 | 70 | 110 | 105 | 60 | 1,550 | 21.9 | 0.91 | 0.17 | 96.9 | 49.80 |
| 48 | 3 | 1 | 4 | — | 135 | — | 110 | — | — | 350 | — | — | — | No analysis | — |

The quantity of circulating phosphoric acid, which always had a concentration of 45 % P₂O₅, was increased to $f = 4$ to 4.4. Of this quantity, $f = 2.7$ to 3 was used for the forming of monocalcium phosphate with half the quantity of phosphate. Calculated on this quantity the factor became in reality $f = 5.4$ to 6. The rest of the phosphate was added to the sludge afterwards.

A quantity of circulating phosphoric acid from $f = 1$ to $f = 1.4$ was added to the sulphuric acid. It should be noted that the phosphoric acid factor f is always calculated on the whole quantity of phosphate taking part in the reaction, whether mixed at once with phosphoric acid or added to the sludge afterwards.

The temperature of the mixed acids was raised to about 135° C. When only 115° C, as in trial Nr 30, the filtering speed was still good, although it should be remembered that during these small trials the sludge was always heated. In a full size process, a temperature of about 135° C will be necessary in the mixed acids if no heat is to be added to the sludge afterwards. When the temperature of the acids was raised to 150° C (trial Nr 44) the result was less good. The final concentration of the mother liquor does not seem to have any influence on the filtering speed.

Some very good yields were attained, as in trial Nr 31. In this case there was a surplus of sulphuric acid so that the mother liquor held 4.26 % SO₂.

Trials Nrs 36—38 were performed without adding sludge from an earlier operation. The filtering speed was practically as good as when sludge was added.

The results of these series are rather good, with varying filtering speeds.

Table 4.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | Min. temp. of sludge °C | Thick-ness of cake mm | Filter- ing speed m ³ /h | Filter surface for production of 40 tons P ₂ O ₅ /24h m ² | Dry cake | | Yield % | Mother liquor % P ₂ O ₅ |
|---------------|----------------------------|------------------|-------|----------------------|----------------|----------------------------------|-------------------------|-----------------------|-------------------------------------|--|--------------------------------------|--|---------|---|
| | mixed with | | total | Phos- phoric acid °C | mixed acids °C | Sludge during main reac- tion °C | | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | Phos- phate | Sul- phuric acid | | | | | | | | | | | | |
| 49 | 3 | 2 | 5 | 20 | 127 | 110 | 105 | 55 | 3,300 | 11.2 | 1.37 | 0.28 | 95.0 | 45.92 |
| 50 | 3 | 2 | 5 | 20 | 133 | 110 | 105 | 55 | 3,900 | 12.7 | 1.21 | 0.10 | 95.8 | 44.07 |
| 51 | 3 | 2 | 5 | 20 | 130 | 110 | 105 | 60 | 3,600 | 13.0 | 1.24 | 0.17 | 96.3 | 43.31 |
| 52 | 3 | 2 | 5 | 20 | 129 | 110 | 95 | 55 | 1,750 | 22.5 | 1.42 | 0.27 | 95.0 | 43.38 |
| 53 | 3 | 2 | 5 | 20 | 136 | 110 | 96 | 62 | 2,300 | 16.3 | 1.84 | 1.73 | 95.8 | 45.88 |
| 54 | 3 | 2 | 5 | 20 | 132 | 110 | 105 | 55 | 4,400 | 9.0 | 1.03 | 0.11 | 95.6 | 43.75 |
| 55 | 3 | 2 | 5 | 20 | 132 | 110 | 98 | 60 | 2,600 | 14.5 | 2.33 | 1.28 | 95.4 | 43.07 |
| 56 | 3 | 2 | 5 | 20 | 132 | 110 | 105 | 62 | 3,700 | 13.7 | 1.20 | 0.11 | 96.2 | 44.06 |

In this series, the phosphoric acid factor was $f = 3$ for the acid mixed with the phosphate and $f = 2$ for the acid mixed with the sulphuric acid, so that the total factor was raised to $f = 5$. Still only half the quantity of phosphate was mixed with phosphoric acid to form monocalcium phosphate sludge and the rest added afterwards.

The results are also rather good. No doubt the increase in circulating phosphoric acid to $f = 5$ has improved the results. The filtering speed varies, however, from 1,750 litres per m² and hour to 4,400 litres.

Table 5.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | Min. temp. of sludge °C | Thick-ness of cake mm | Filter- ing speed m ³ /h | Filter surface for production of 40 tons P ₂ O ₅ /24h m ² | Dry cake | | Yield % | Mother liquor % P ₂ O ₅ |
|---------------|----------------------------|------------------|-------|----------------------|----------------|----------------------------------|-------------------------|-----------------------|-------------------------------------|--|--------------------------------------|--|---------|---|
| | mixed with | | total | Phos- phoric acid °C | mixed acids °C | Sludge during main reac- tion °C | | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | Phos- phate | Sul- phuric acid | | | | | | | | | | | | |
| 57 | 1.9 | 1.9 | 4.8 | 20 | 130 | 110 | 105 | 65 | 5,100 | 7.5 | 1.22 | 0.18 | 96.0 | 44.40 |
| 58 | 2.9 | 1.9 | 4.8 | 20 | 130 | 110 | 106 | 60 | 7,000 | 5.5 | 1.38 | 0.15 | 95.3 | 44.60 |
| 59 | 2.9 | 1.9 | 4.8 | 20 | 130 | 110 | 100 | 65 | 4,300 | 8.7 | 3.92 | 2.00 | 96.3 | 45.61 |
| 60 | 2.9 | 1.9 | 4.8 | 20 | 132 | 110 | 107 | 65 | 5,600 | 7.1 | 1.42 | 0.30 | 96.0 | 44.83 |
| 61 | 2.9 | 1.9 | 4.8 | 20 | 132 | 110 | 107 | 65 | 5,900 | 6.7 | 1.28 | 0.24 | 96.4 | 44.49 |
| 62 | 3 | 2 | 5 | 20 | 113 | 110 | 106 | 62 | 7,700 | 5 | 1.38 | 0.02 | 94.8 | 44.20 |
| 63 | 3 | 2 | 5 | 20 | 130 | 110 | 108 | 65 | 6,500 | 5.9 | 1.22 | 0.05 | 95.5 | 44.37 |

It was thought that the uneven results in trials Nos 49—56 might depend on the concentration of the circulating phosphoric acid, so that this concentration was lowered to 43 % P₂O₅. In all other respect the conditions were the same as in table 4.

The results were exceedingly good, even when the total factor was lowered to $f = 4.8$. The best results were obtained with $f = 5$. The monocalcium phosphate sludge was thinner and could be poured into the sulphuric acid mixture more easily.

B. A mixture of phosphate and phosphoric acid was allowed to solidify and the pulverized product was added to sulphuric acid mixed with phosphoric acid

It should be noted that these trials were made at an earlier stage than the trials in tables 4 and 5, before it was found that an increase of the circulating phosphoric acid to

$f = 5$ and a lowering of its concentration to 43 % and a stabilizing effect on the process and also resulted in a remarkable increase in the filtering speed. Consequently the results obtained in tables 6 and 7 should be compared, not with tables 4 and 5, but with table 3. It is believed that further trials with solidified monocalcium phosphate and circulating phosphoric acid with $f = 5$ and 43 % P_2O_5 will result in even as good filtering speed as shown in table 5.

Table 6.

| Trials Num ber | Phosphoric acid factor (f) | | | Temperature of | | | | Thick- ness of cake mm | Filter- ing speed m ² /h | Filter surface for pro- duction of 40 tons P ₂ O ₅ /24h m ² | Dry cake | | Yield % | Mother liquor % P ₂ O ₅ |
|----------------------|-------------------------------|------------------------|-------|-------------------------------|----------------------|---|-------------------------------------|------------------------------------|--|---|--|---|------------|---|
| | mixed with | | total | Phos- phoric acid °C | mixed acids °C | Sludge during main reac- tion °C | Mtu- temp. of sludge °C | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | Phos- phate | Sul- phuric acid | | | | | | | | | | | | |
| 64 | 2.6 | 1.8 | 4.4 | 20 | 135 | 110 | — | 50 | 3,200 | 10.8 | 1.42 | 0.29 | 95.7 | 46.00 |
| 65 | 2.6 | 1.4 | 4 | 20 | 125 | 110 | — | 55 | 2,900 | 12.7 | 1.08 | 0.19 | 95.3 | 48.12 |
| 66 | 2 | 2 | 4 | 20 | 140 | 110 | 110 | 50 | 2,600 | 13.1 | 2.10 | 0.31 | 93.2 | 46.45 |
| 67 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 48 | 4,000 | 9.0 | 1.24 | 0.17 | 90.3 | 42.22 |
| 68 | 2.6 | 1.4 | 4 | 60 | 130 | 110 | — | 48 | 2,800 | 13.0 | 1.73 | 0.41 | 95.3 | 43.63 |
| 69 | 2.6 | 1.4 | 4 | 60 | 135 | 110 | — | 55 | 2,700 | 13.3 | 1.48 | 0.22 | 95.3 | 46.80 |
| 70 | 2.6 | 1.4 | 4 | 20 | 138 | 110 | 105 | 50 | 2,100 | 16.6 | 1.07 | 0.23 | 96.0 | 46.62 |
| 71 | 2.6 | 1.4 | 4 | 20 | 136 | 110 | — | 55 | 2,100 | 16.0 | 1.62 | 0.26 | 91.6 | 49.08 |
| 72 | 2.6 | 1.4 | 4 | 20 | 138 | 110 | 100 | 55 | 1,800 | 18.0 | 1.22 | 0.33 | 96.6 | 48.81 |
| 73 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 50 | 1,650 | 21.0 | 1.25 | 0.23 | 96.5 | 47.07 |
| 74 | 2.6 | 0.9 | 3.5 | 20 | 140 | 110 | 110 | 60 | 1,000 | 31.0 | 1.21 | 0.25 | 96.3 | 48.20 |
| 75 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 55 | 1,700 | 20.0 | 1.66 | 0.21 | 94.1 | 48.92 |
| 76 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 55 | 2,900 | 12.1 | 1.08 | 0.18 | 96.4 | 44.25 |
| 77 | 2.6 | 1.4 | 4 | 20 | 132 | 110 | 110 | 50 | 3,000 | 12.3 | 1.01 | 0.14 | 96.7 | — |
| 78 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 60 | 2,300 | 14.3 | 1.25 | 0.16 | 96.2 | 46.48 |
| 79 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 50 | 2,300 | 14.5 | 0.86 | 0.12 | 97.2 | 43.66 |
| 80 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 55 | 1,500 | 13.0 | 0.91 | 0.10 | 96.9 | 46.77 |
| 81 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 100 | 45 | 3,300 | 10.1 | 1.20 | 0.16 | 95.3 | 43.43 |
| 82 | 2.6 | 1.4 | 4 | 20 | 135 | 110 | 110 | 60 | 2,600 | 12.1 | 1.69 | 0.22 | 95.5 | 47.44 |

In all these trials, the whole quantity of phosphate was mixed with phosphoric acid in a quantity of $f = 2.6$ except in trial Nr 66 when it was lowered to $f = 2$. The filtering speed was not reduced, but the yield was lowered in this trial.

During most of the trials, the phosphoric acid and the phosphate was vigorously mixed during 45 seconds. The reaction mass rose to thrice its volume, and after about 2 minutes it had solidified to a honey-combed cake with a volumetric gravity of only about 0.5. After 10—15 minutes of solidification the cake was scraped off and added in portions once a minute during 15 minutes to the sulphuric acid, which was mixed with phosphoric acid $f = 0.9$ to 1.8.

In trial No 64 the circulating phosphoric acid was increased to $f = 4.4$ which gave a filtering speed higher than the average, and in trial Nr 74 it was lowered to $f = 3.5$ which gave a lower speed than the other trials.

During these trials no sludge from an earlier trial was added in the process except in trials Nrs 76—80. No effect was apparent.

The result seem to be more even than in table 3.

Table 7.

| Trials Number | Phosphoric acid factor (f) | | | Temperature of | | | Min. temp. of sludge °C | Thick ness of cake mm | Filtering speed m ³ /h | Filter surface for production of 40 tons P ₂ O ₅ /24h m ² | Dry cake | | Yield % | Mother liquor % P ₂ O ₅ |
|---------------|----------------------------|---------------------|-------|--------------------|----------------|--------------------------------|-------------------------|-----------------------|-----------------------------------|--|--------------------------------------|--|---------|---|
| | mixed Phosphate | with Sulphuric acid | total | Phosphoric acid °C | mixed acids °C | sludge during main reaction °C | | | | | tot. P ₂ O ₅ % | water sol. P ₂ O ₅ % | | |
| | | | | | | | | | | | | | | |
| 83 | 1.3 | 2.7 | 4 | 20 | 134 | 110 | 110 | 55 | 3,100 | 12 | 1.63 | 0.41 | 95.3 | 42.77 |
| 84 | 1.1 | 1.7 | 3 | 20 | 135 | 110 | 105 | 60 | 1,700 | 20 | 2.07 | 0.58 | 93.5 | 41.80 |
| 85 | 1.1 | 1.7 | 4 | 20 | 130 | 110 | 108 | 50 | 4,100 | 9 | 1.64 | 0.40 | 93.5 | 42.77 |
| 86 | 1.1 | 1.7 | 4 | 20 | 132 | 110 | 110 | 55 | 2,700 | 13 | 1.33 | 0.33 | 96.2 | 43.71 |

In these trials half the quantity of the phosphate was transformed to monocalcium phosphate by treating it with phosphoric acid in a quantity of $f = 1.3$, and the rest of the phosphate was added to the final sludge after 1 hour 20 minutes. The results were slightly better than the trials in table 6, with the exception of trial Nr 84, in which the circulating phosphoric acid was only $f = 3$. The filtering speed was considerably lessened and also the yield.

Observations and Results

In order to perform the Anhydrite process with the maximum of filtering speed, large quantities of phosphoric acid should be circulated in the process. The best results were obtained with $f = 5$. Although such large quantities are circulated in the process, the effective filter area can be kept as low as in the Dihydrate process.

In all cases the phosphate, or part of it, should first react with phosphoric acid and the product thus received, partly consisting of monocalcium phosphate, should afterwards be added to heated sulphuric acid, or, preferably, to a heated mixture of sulphuric and phosphoric acid.

There are two ways of performing the Anhydrite process: either to keep the monocalcium phosphate in a fluid state by adding a surplus of phosphoric acid; or to let the monocalcium phosphate solidify and to add the pulverized product to the acid or acids. In both cases good results can be obtained.

Only half the quantity of phosphate is needed for the making of monocalcium phosphate. The rest can be added afterwards. This is recommended when the monocalcium phosphate should be added to the sulphuric acid as a sludge, but it could be done also when the monocalcium phosphate is allowed to solidify. The rest of the phosphate should be added to the final sludge after about $\frac{1}{4}$ of the reaction time. In this way the apparatus for the making of monocalcium phosphate can be given a smaller size.

The filtering speed is considerably increased if the strength of the circulating phosphoric acid is lowered from 45 % P₂O₅ to 43 % P₂O₅. Once the main part of the anhydrite crystals is formed, the strength of the mother liquor can be heightened to 45 % P₂O₅ or more. In a full-sized plant, the high temperature of the reaction will cause a certain evaporation and concentration of the mother liquor. It will also be necessary to cool the sludge before the filtration to a temperature of 60—80° C, which probably can be done by circulating sludge through a small tower under vacuum. This will give an increased concentration of the mother liquor.

If the mother liquor has 45 % P_2O_5 , the first filtrate, the product, can be obtained with the same strength. The second filtrate, the circulating phosphoric acid, which for $f = 5$ contains 5 times the quantity of P_2O_5 in the product, can be allowed to sink to 43 % P_2O_5 ; the ensuing filtrate fractions, used as wash liquids, should hold about 35, 20 and 5 % P_2O_5 . In all, 5 filtrates should be taken. Such filtrations can only be performed on horizontal filters of special design. Part of the heat necessary for the concentration of the circulating phosphoric acid during the process from 43 % to 45 % P_2O_5 will be taken from the reaction heat and the rest of the heat required from the preheating of the acids.

The yield will be higher if the phosphate is more finely ground, also if there is a surplus of sulphuric acid, but very little will be gained by a longer reaction time than 4 hours.

The monocalcium phosphate should be allowed a reaction time of about 10—15 minutes before being added to the sulphuric acid. An aged and seasoned triple superphosphate does not give good crystals. The reason of this is not yet known.

There are three points at which froth appears in the process. The first is when the phosphate is mixed with phosphoric acid. This acid should be cooled down to a low temperature which will diminish the froth. If the monocalcium phosphate is allowed to solidify, the quantity of phosphoric acid being $f = 2.6$, counted on the actual phosphate with which it reacts, no real froth is formed but the volume of the mixture rises as it solidifies to three times its first volume. The second point is when the monocalcium phosphate, in sludge or in a solid state, is added to the sulphuric acid. The froth then takes about the same volume as the underlying sludge. The third point is when the second half of the phosphate is added to be final sludge. The later this addition is made the less froth is formed. As far as can be seen from the trials, the digesters should hold a volume double the size of the sludge they contain. The simplest way to avoid difficulties with the froth seems to be to make the vessels large enough. This refers to the use of morocco phosphate. In all cases the mixing of the phosphate with acids or sludge should be performed in such a manner that part of the phosphate is not held up by the froth, as otherwise the yield will be reduced.

The crystals should be studied in the microscope. Small crystals, evenly dispersed, show bad filtering capacities. Small crystals, in agglomerations, may give a high filtering speed. The best are the large-sized, unagglomerated crystals, flat and square, with a right-angle intake in one corner.