

ISMA* Technical Conference

Edinburgh, United Kingdom

14-16 September 1965

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

FULL SCALE PRODUCTION OF SEMIHYDRATE PHOSPHORIC ACID WITH 42% P₂O₅

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Introduction

There are two possibilities for the production of phosphoric acid with a concentration over 42% P₂O₅ without evaporation: the anhydrite (CaSO₄) and the semihydrate⁵ (CaSO₄ · 1/2 H₂O) processes. The operating temperature for the anhydrite⁴ process at a concentration of 42-45% P₂O₅ is 120-130°C, and for the semihydrate process it is sufficient to keep the temperature at about 100°C (see figure 1) (1).

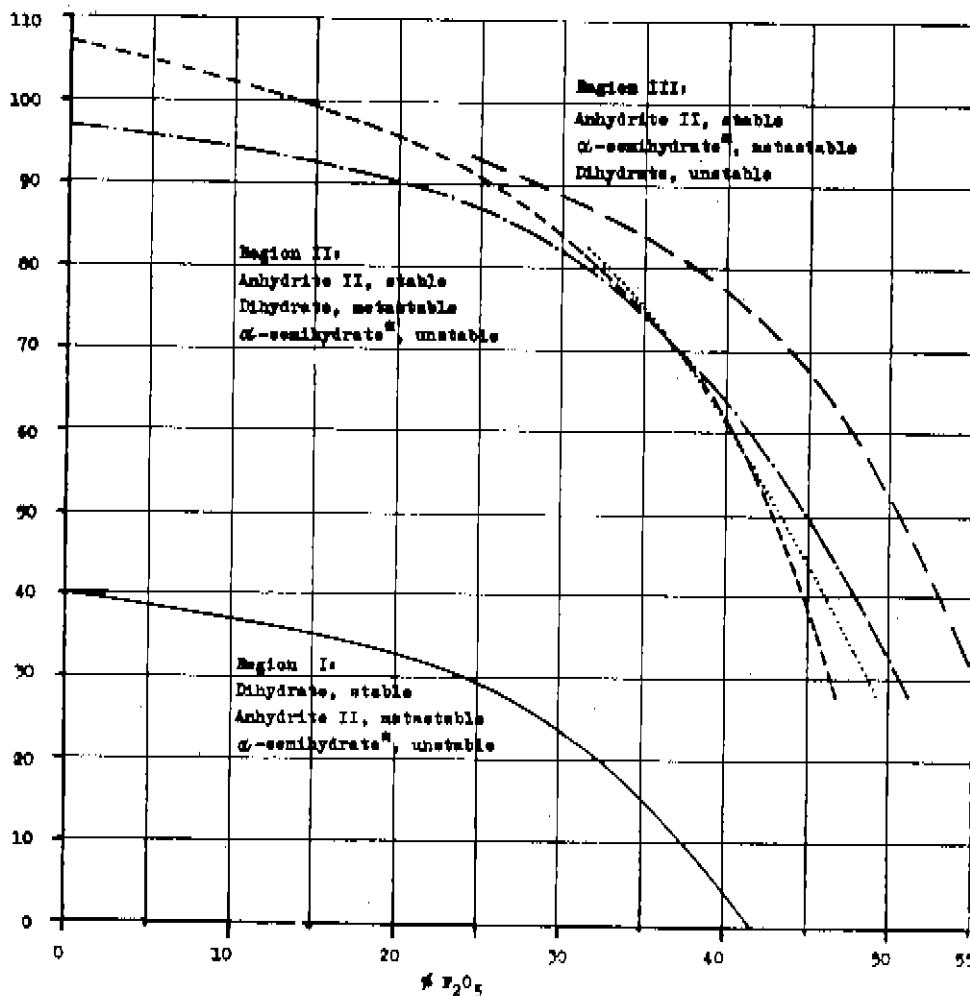
From 1956 to the end of 1963 we have produced acid with 42% P₂O₅ in one step in our phosphoric acid plant in Landskrona. During the first few years, we used the anhydrite process, but we encountered certain technical problems. During this time, our research and development department made an investigation to find out if there was any possibility of producing strong phosphoric acid by means of the semihydrate process. After a lot of tests, we found that we might favourably change over to the semihydrate process, and this was done in 1959. The main reasons for this were the following:

- a) The maintenance costs were higher for the anhydrite process, as a consequence of the severe corrosion of the construction materials at 130°C.
- b) With only the reaction heat it was impossible to reach an operating temperature of 120-130°C in the slurry. Therefore the reactors had to be indirectly heated by steam for the anhydrite process. When using the semihydrate process the reaction heat was high enough to keep the temperature of the slurry at 100°C.
- c) For heating the slurry to 130°C in the first reactor it was necessary to run all the feeders intermittently, but for the lower temperature (100°C) required by the semihydrate process we were able to run the whole system continuously.

Description of equipment

The plant was built for the anhydrite process, and therefore some equipment was not necessary for producing semihydrate, e.g. steam-jacketed reactors, heaters for sulphuric acid, and scoop-

Temperature °C



DIHYDRATE—ANHYDRITE II

———— thermodynamically calculated equilibrium curve from vapor pressure of pure phosphoric acid solutions using the thermodynamic relations of Kelley et al.

DIHYDRATE—α-SEMIHYDRATE*

———— thermodynamically calculated equilibrium curve from vapor pressure of pure phosphoric acid solutions using the thermodynamic relations of Kelly et al.

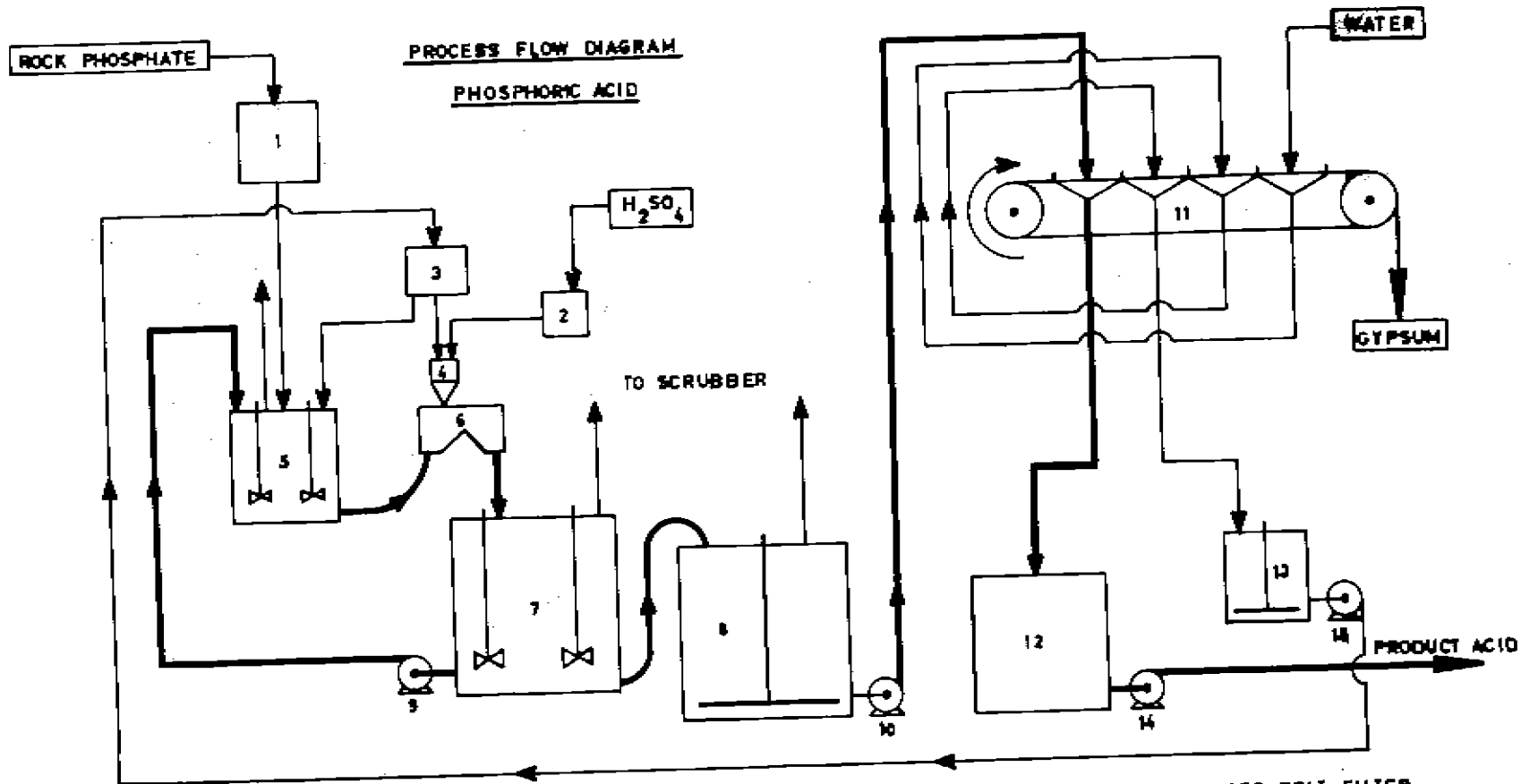
----- Multbom-Lehrcke's curve

..... equilibrium curve from solubility measurements by Taperova and Shul'gina

- . - . - Sanfourche's curve

The asterisk indicates an over-stoichiometric crystal water content

Figure 1. The transitions dihydrate—α-semihydrate* and dihydrate—anhydrite II in phosphoric acid solutions



- 1 BATCH WEIGHER
- 2 ROTAMETER
- 3 DISTRIBUTION BOX
- 4 MIXER
- 5 REACTION TANK

- 6 OVERFLOW
- 7 REACTION TANK
- 8 FILTER FEED TANK
- 9 SLURRY PUMP
- 10 SLURRY PUMP

- 11 LANDSKROMA RUBBER BELT FILTER
- 12 PRODUCT ACID TANK
- 13 RETURN ACID TANK
- 14 PRODUCT ACID PUMP
- 15 RETURN ACID PUMP

FIGURE 2.

feeders for sulphuric acid and return acid. The description given below includes only the equipment we had in 1963 (see figure 2).

1. Feeders

- a) The rock phosphate was metered by an automatic batch weigher.
- b) The sulphuric acid was metered by a rotameter, which was connected to an automatic control valve for keeping a constant flow.
- c) The return acid from the last washing section of the filter was metered by a distribution box.

2. Reaction station

This consisted of three reaction tanks with agitators and with respective volumes of 10, 55 and 55 m³, totalling 120 m³.

The first tank in the reaction system had a volume of about 10 m³. Two strong agitators were erected to get a good premixing of the ground phosphate rock and the recirculated slurry. To get a fluid slurry some of the return acid had to be added to the premixer. The sulphuric acid, diluted with the rest of the return acid, was fed to the reaction system in the overflow from the first reaction tank (premixer).

The second reaction tank had a volume of about 55 m³ and was equipped with two agitators of the same size, of the Dorcco-mixer type. Two foam breakers were also erected in the first and second tanks.

The third tank was used only as a filter feed tank, and the volume was also about 55 m³, but normally it was kept only half full and was supplied with a simple paddle agitator.

The construction material of the reaction tanks were steel, rubber lined with neoprene, one layer of acid proof bricks, 20 mm, and one inner layer of carbon bricks, 40 mm. The agitator shafts were made of rubber lined steel, and the impellers were of an acid proof alloy (20% Cr, 24% Ni, 3% Mo and 2% Cu). Even polypropylene was used with good results as a construction material for the impellers.

The filter feed tank, 55 m³, was made of wood with an inner layer of lead, and the paddle agitator was made of steel, protected with lead.

The recirculated slurry was pumped from the second tank to the first one. The semihydrate slurry cannot be pumped

by a centrifugal pump, because the crystals would be crushed by the pump impellers at a normally high revolution. We therefore used air-pressure pumps (Tungstone) to prevent the crystals from being damaged. The pumps were made of rubber lined steel, and neoprene was also used in this case because of the high temperature.

Fume system

The reaction tanks were held at a small negative pressure by an exhaust fan, which delivered the fumes to a scrubber (AUT 120 Pauls Kestner).

Filter station

In the beginning, three travelling pan filters of 16 m² each was installed in the plant, but in 1958 we changed one of them₂ for a Landskrona rubber belt filter with a filter area of 15 m², and in 1962 a second belt filter replaced the two remaining pan filters. The reasons for changing to these filters were better efficiency and lower maintenance costs.

One filter of 15 m² was more than enough for the production. When one filter was in operation the other one was washed with hot water in order to clean the filter cloth, the vacuum box and all the pipes and rubber hoses which were connected to the filter.

Some process data

Raw material

Khouribga phosphate rock with a P₂O₅ content of about 34% and ground to 80% < 100 mesh was used.

The sulphuric acid had a concentration of about 93% H₂SO₄.

The return acid had a concentration of about 37% P₂O₅.

Reaction

The highest feeding rate we used was 4,200 kg/h of ground phosphate rock, which is about 35 metric tons per day of P₂O₅. The reaction volume was 65 m³, not including the filter feed tank. This corresponds to a reaction time of 12 h. The normal reaction time for the semihydrate process is 8-9 h, and so there was a possibility of increasing the capacity. The temperature was kept between 95-100°C, and when starting up the process we used direct steam for heating the slurry to this temperature.

The sulphuric acid content of the mother liquor was between 3,0 and 3,5% by weight, and the feeding rate was about 2,8 ton/ton P₂O₅.

The return acid had a concentration of about 37% P₂O₅, and the rate was adjusted in accordance with the concentration of the

product acid.

The recirculation of the slurry was about 6 times the production quantity.

The foam breakers were sufficient to eliminate foaming in the reactor system and no anti-foaming application was necessary.

Filtration

The losses of water-soluble P_2O_5 in the filter cake were very high: about 6% of the total P_2O_5 for the travelling pan filter, and 3,8% for the Landskrona rubber belt filter. The difference in the efficiency of the two types of filter is explained by the easier and better washing of the filter cake and the filter cloth on the rubber belt filter. In addition, the capacity of the rubber belt filter was higher than that of the travelling pan filter, i.e. 3 ton P_2O_5/m^2 24 h compared with 1,5 ton P_2O_5/m^2 24 h.

The filter cake was washed with water and with two, sometimes three wash acids with the following concentrations: 5%, 20% and 35% P_2O_5 .

Summary

With the semihydrate process it is possible to get an acid concentration of 42% P_2O_5 without any evaporation, and the equipment is about the same as for a plant using the dihydrate process, except for the cooling system. The maintenance costs for the semihydrate process are higher than for the dihydrate process because of the corrosion problems at a higher working temperature and concentration. A plant for the semihydrate process must be built for easy cleaning, because the small semihydrate crystals and silicates clog the filter cloth and pipelines very quickly.

The filter area for a semihydrate process must be nearly twice as big as for a dihydrate plant.

As mentioned above, from 1959 to 1963 the plant produced phosphoric acid using the semihydrate process with comparatively good success. In 1963 a new NPK-plant was started up and it was necessary to increase the production of phosphoric acid. The phosphoric acid plant was then rebuilt according to the dihydrate process, as a concentration of 30% P_2O_5 was sufficient.

1. Dahlgren, S-E: Physico-Chemical Background of Phosphoric Acid Manufacture by Wet Processes. Acta Polytechnica Scandinavica (Acta P. 271/1960), Chemistry including Metallurgy Series 7, Stockholm 1960.

DISCUSSION

MR. R. HAKANSSON (A/B Förenade Superfosfatfabriker, Sweden)

In our phosphoric acid plant in Landskrona we used the semi-hydrate process for five years for producing acid with 42% P_2O_5 without evaporation. The main reasons for changing from the anhydrite to the semihydrate process were as stated on page 1 of my paper. At first, when we were still using the travelling pan filters, we had very high losses of water soluble P_2O_5 in the filter cake. This was because of insufficient washing of the filter cloth. But on the Landskrona belt filter it is easy to wash the filter cloth on both sides and also to keep the rubber belt free from semihydrate with water during operation. If the semihydrate stays too long on the filter, it will hydrate and clog the filter very quickly. And, as I have indicated in the paper, we have produced phosphoric acid using the semihydrate process with comparatively good results.

MR. G. MRKUSIC (Bosveld Kunsmis (EDMS), South Africa) :

The advantage of producing phosphoric acid of 42% P_2O_5 concentration in one step without evaporation has repeatedly exercised the imagination and interest of phosphoric acid research and development workers in many countries. The results so far obtained, particularly with the semihydrate process, justify the maintenance of this interest until the problem can be solved satisfactorily from the economic and operational points of view. Mr. Hakansson's paper is an excellent contribution in this direction.

It would appear that his company's semihydrate plant was operated relatively successfully from 1959 to 1963. In order to assess this, it would be useful if Mr. Hakansson could give an indication of plant utilisation or of the scheduled and forced-down time during the operating period. In addition, what was the approximate total average plant P_2O_5 efficiency when operating with the Landskrona belt filter?

If our interpretation of Mr. Hakansson's paper is correct, we would say that, in comparison with the dihydrate process, the capital and operating costs of the reaction station are lower with the semihydrate process. This process requires no installation for dilution and cooling of the sulphuric acid and no equipment for the cooling of phosphoric acid slurry. The filtration losses of 3.8% P_2O_5 with the Landskrona filter is, in our opinion, not alarmingly high. At first sight, the capacity of this filter of 3 tons $P_2O_5/m^2/24$ hours does not compare favourably with filter capacities with the dihydrate process. However, the comparison changes very much in favour of the semihydrate process, especially for the point of view of capital and operating costs, when the concentration of the product phosphoric acid is taken into account. We would be very grateful if Mr. Hakansson could indicate whether his company or, to his knowledge, any other organisation in the world, are

presently engaged on development work relating to the semi-hydrate process and, if so, what results have been obtained so far.

MR. HAKANSSON : The extraction losses were about 2.2%, giving an overall efficiency of 94% in this plant. As far as plant utilisation is concerned, I do not have any precise figures with me but I believe it was about 50-60%, and the reason for this was that we had no need of more phosphoric acid at Landakrona at that time. My company did a lot of research on the semihydrate process at the time, but I do not have the detailed results with me; and I do not know whether other companies have carried out similar work. But I believe that the commercial prospects for the semihydrate process are good. There are, of course, a number of problems involved, and with higher maintenance costs the efficiency of the semihydrate process is lower than that of the dihydrate process. Much depends on whether one requires a weak acid or a stronger acid without evaporation.

MR. P. G. GLIKIN (Simon-Carves Ltd., U.K.) : Has Mr. Hakansson any information on the frequency of cleaning the filter when operating with the semihydrate process? How long was the filter on stream before washing? What was the life of the filter cloth?

Is the semihydrate sufficiently stable not to hydrate when washing?

What was the method of disposal of the semihydrate?

Could Mr. Hakansson confirm that the loss of 3.8% P_2O_5 in filtration refers to the P_2O_5 in the phosphate rock used and not to the P_2O_5 in the waste gypsum?

MR. HAKANSSON : We were operating only one filter. We washed it with hot water after every 24 hours of operation for about 8 hours. We used a multi-filament terylene cloth. The life of such a cloth was about 4 months.

The semihydrate is, indeed, sufficiently stable not to hydrate when washing. After Filtration it is slurried in water and pumped to store: we do not use it for anything. It contains 5 - 10% gypsum.

The 3.8% P_2O_5 loss is calculated with reference to the phosphate rock.

MR. A. M. BRZOZOWSKI (Mathew Hall Engineering Ltd, U.K.): The filtration difficulties encountered appear to be similar to the experience of I.C.I. about 35 years ago when they tried to produce phosphoric acid in hemihydrate form. Mr. Hakansson and his colleagues seem to have overcome most of these difficulties. However, it would be interesting to learn more of Mr. Hakansson's

experience in this respect.

In particular, what has been done to improve crystal size and reduce cloth blinding? Also, in Fig. 2, crystal discharge is shown as gypsum. Presumably this is used as a general term, as the crystals are $\text{CaSO}_4 \frac{1}{2} \text{H}_2\text{O}$ and not $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Has a rotating pan filter been tried? Presumably it would give similar results to a travelling pan filter, but possibly it might not.

With regard to silicate blinding of the filter cloth, it might be worth investigating the reaction of silicates with fluorine and the distribution of the fluorine to vent gas, product acid and filter cake. If Mr. Hakansson has done this, I should be interested to hear his results.

Was the phosphate rock calcined or uncalcined? It would be interesting to hear Mr. Hakansson's views on the behaviour of calcined and uncalcined rock in phosphoric acid production by the semi-hydrate process.

Mr. Hakansson states that maintenance costs were high for the anhydrite process. Could he give figures to illustrate this? Could these costs be reduced by using different construction materials?

MR. HAKANSSON : With regard to the improvement of crystal size, I do not have our laboratory report with me and am therefore unable to answer.

We have no experience of a rotating pan filter.

We used uncalcined Khouribga phosphate rock, and we have not tried using calcined rock.

It would be very difficult to give significant figures for maintenance costs, because production was not continuous during the operation of either anhydrite or the semi-hydrate process.

MR. R. BAUWENS (Ets. Kuhlmann, France) : You recycle a considerable quantity of 37% phosphoric acid. Is this necessary in order to have a fluid slurry and well-formed crystals or is it the result of the operation of your filter with the slurry in question?

MR. HAKANSSON : This recycling of 37% acid is necessary for attaining the final concentration of the product acid. In this way, we can also achieve a fluid slurry and well-formed crystals.

MR. BAUWENS : Do the semi-hydrate crystals in your process take the form of isolated crystals or agglomerates ?

MR. HAKANSSON : They are agglomerated.

MR. BAUWENS : Is the strong sulphuric acidity in your solutions absolutely necessary to achieve a good reaction yield ? Do you not think that the reaction time of 9 hours which you mention is due precisely to this strong sulphuric acidity ?

MR. HAKANSSON : The sulphuric acid strength is required for the heat balance. Using the strong acid and diluting it with recycled acid, we do not need to use additional heat during operation. We have not tried a weaker acidity in the reaction, and so I do not know whether this would reduce the reaction time.

MR. M. ROUBINET (Péchiney-St. Gobain, France) : In view of your experience, is your choice of the semi-hydrate process in preference to the anhydrite process definite ?

MR. HAKANSSON : Yes, our preference for the semihydrate process was quite definite, because of the lower operational temperature, lesser corrosion and yet with almost the same acid concentration as with the anhydrite process.

MR. ROUBINET : You say in your text that you carry out a pre-reaction in a tank. I should like to know whether this pre-actor is a traditional feature for you or whether it is a key item in your process.

MR. HAKANSSON : The pre-mixer is necessary in order to wet the ground phosphate rock before its reaction with the sulphuric acid and thus to prevent blocking.

MR. ROUBINET : You mention that the semi-hydrate does not re-hydrate on the filter. Do you know the time it takes before the semi-hydrate turns to gypsum when it is discharged dry ?

MR. HAKANSSON : As I said before, there is no rehydration on the filter; nor does this occur in the pipeline through which the semihydrate is pumped to store. The pipeline is about 1200 m. long. Of course, it happens in the store. We have made no tests, but I think it takes several hours before rehydration occurs.

MR. ROUBINET : In your summary you write: "The filter area for a semihydrate process must be nearly twice as big as for a di-hydrate plant." At what concentration have you made this comparison and with what phosphate rock ?

MR. HAKANSSON : We used Khouribga phosphate, with a concentration of 32% P_2O_5 in the acid.

MR. ROUBINET : With regard to sulphuric acid consumption per ton of P_2O_5 produced, have you any figures comparing the semi-hydrate and di-hydrate processes ?

MR. HAKANSSON : As far as I know, sulphuric acid consumption is almost the same for both processes. Perhaps the dihydrate process may use very slightly less.

MR. W. C. WEBER (Dorr-Oliver, U.S.A.) : I have firstly three questions relating to the character of the calcium sulphate crystals, which, as you have said, are agglomerates.

What is the character of the agglomerates ? Are they flocculated aggregates of small crystals, or are they cemented together or twinned ?

Were you ever able to obtain reasonably large-sized individual crystals, as shown in Figs. 1 - 3 in Mr. Bauwens' paper ? In some work carried out by Dorr-Oliver, we obtained agglomerates at low sulphate levels, together with individual crystals, in the range of 1 - 3% sulphates. Above this point, at 38% P_2O_5 and 85°C we started to get anhydrite.

Do you have any anhydrite in your slurry, when operating the hemi-hydrate process, and if so, how is it controlled ?

MR. HAKANSSON : I am sorry that I do not have our research data available on the nature of the crystals, but normally we did not obtain such good crystals as are shown in Mr. Bauwens' photographs. Again, as far as I know, we never encountered any anhydrite in the slurry, and I am unaware of any methods of testing.

MR. WEBER : On page 6, you state that even with the improved Landskrona filter, the water soluble losses in the cake were 3.8%. No mention is made of the insoluble losses. We all know that the most serious loss in phosphoric acid manufacture is the so-called co-precipitation of crystal lattice loss which is usually measured as citrate soluble P_2O_5 . You gave the total losses in the previous discussion, but you did not sub-divide this to give the unattacked and co-precipitation losses. I should therefore like to ask how much citrate soluble but water insoluble P_2O_5 loss do you have in your semihydrate. Secondly, what are the comparative figures for the anhydrite process you formerly operated and the dihydrate process you are now operating ? What factors affect this loss; e.g. acid strength, the level of excess sulphates etc.. What are the water soluble losses with your present dihydrate process ?

MR. HAKANSSON : As I have said previously, the water insoluble losses with our semihydrate process were 2.2%, but we have not broken this down to analyse the citrate soluble

loss. Similarly, we have not checked this point for either the anhydrite or the dihydrate process. The water soluble loss for the dihydrate process we are now operating is 0.8 - 1.0%.

MR. WEBER : In view of the higher maintenance costs for the semihydrate process, as well as its higher water soluble P₂O₅ losses and much greater requirement for filtration capacity, do you feel that the saving in evaporation from 31% to 42%, amounting to about 0.8 ton of water per ton P₂O₅, justifies the higher costs and other disadvantages of the semihydrate process?

Do you have any relative figures on fluorine distribution between fumes evolved, acid produced and filter cake for the anhydrite, semihydrate and dihydrate processes ?

MR. HAKANSSON : As far as the economic justification of the various processes is concerned, this depends on various local factors and I do not have our figures with me.

As far as the fluorine distribution is concerned, we have checked this for the dihydrate process, but not for the other two processes. But unfortunately I do not have any figures with me.

MR. J. FROCHEN (Pierrefitte-Bassens, France) : Have any trials been made with a phosphate other than that of Khouribga ? If so, what were the results ?

MR. HAKANSSON : Our research laboratories have tested other phosphates than Khouribga phosphate, but I do not have their results available with me. In production we have used only Khouribga phosphate.

MR. FROCHEN : My second question concerns di-hydrate recrystallisation on the filter. You have said that none occurs, but at the same time you mention that it is necessary to wash the filters every day. Are these two statements not incompatible ?

MR. HAKANSSON : The reason why we do not have rehydration is because we do, indeed, wash the filters thoroughly and frequently. If washing is insufficient, the semihydrate stays in the cloth and in the pipelines and is then able to rehydrate.