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PRODUCTION OF PURE CALCIUM SULPHATE HEMI-HYDRATE

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1. Introduction

It is generally known that phosphoric acid manufacture leads to the production of large amounts of calcium sulphate. In the main, this material is today discarded as a waste product, partly at considerable cost, a smaller percentage being utilised as a raw material for the construction industry (gypsum and cement).

Increasing interest attaches to further processing of the calcium sulphate. This is due, on the one hand, to the fact that the various industrial countries have issued more stringent environmental laws which make it more difficult to get rid of the calcium sulphate, while on the other hand the partial exhaustion of gypsum deposits suitable for mining means that "waste gypsum" is gaining in importance also from the point of view of the gypsum manufacturers.

Whereas synthetic gypsum has the advantage of a more homogeneous composition than natural gypsum, it also entails considerable disadvantages by comparison with the latter :

1. higher water content
2. acid impurities which cannot be removed by washing alone
3. more or less colouration, according to the type of phosphate used.

The above main disadvantages mean that the synthetic gypsum must be purified, neutralised and burnt prior to further processing (burning, which is necessary because the water content is higher than that of natural gypsum, entails high costs).

Recently, phosphoric acid processes have been developed which yield the calcium sulphate direct in such a form as to enable it to be utilised in the construction and cement industry without much preparation. These processes are, on the one hand, two-stage processes for the production of phosphoric acid, in which the calcium sulphate is first precipitated as hemi-hydrate, whereupon the hemi-hydrate is converted into dihydrate in a second stage, and, on the other hand, processes in which the calcium sulphate is first precipitated as dihydrate, the latter being converted into hemi-hydrate as the end product in a second stage. As a result of this recrystallization the calcium sulphate produced in the process is obtained with only minor impurities.

Single-stage phosphoric acid processes based on the dihydrate process or the hemi-hydrate process produce only relatively impure calcium sulphate, which has to be purified prior to further processing.

From the gypsum manufacturers' point of view calcium sulphate hemi-hydrate is more valuable than dihydrate, since the energy required for burning the product is considerably smaller. This is the case even if the hemi-hydrate is rehydrated to dihydrate without further water, since in that case the water attaching to the hemi-hydrate is consumed thus yielding a relatively dry dihydrate.

II. Considerations and tests relating to the manufacture of pure calcium sulphate hemi-hydrate

At the Embsen works of VEBA-CHEMIE AG (app. 50 km to the South of Hamburg) tests aiming at the production of pure calcium sulphate hemi-hydrate were started in 1969. These tests were carried out for the following reason:

At the Embsen works phosphoric acid is produced in two phosphoric acid plants in accordance with the dihydrate process. The acid produced is then further utilised for the production of compound fertilizers. The impure gypsum resulting from the phosphoric acid process is stockpiled. We considered whether it is possible to decompose the rock phosphate in one of our two phosphoric acid plants, using nitric instead of sulphuric acid, and to precipitate the calcium ions as calcium sulphate with the aid of ammonium sulphate. This solution had considerable economic appeal since at that time ammonium sulphate being a by-product of the fibre industry was available cheaply in large amounts. The following objectives were, if possible, to be achieved by the new process :

1. Maximum efficiency from the point of view of phosphate and nitrogen losses,
2. In addition, the production of pure calcium sulphate capable of being further processed, to the greatest extent possible, without further purification,
3. Favourable water economy from the point of view of complete fertilizer production, i.e. additional evaporation was to be avoided.

The above requirements - especially in connection with the water economy - led to the conclusion that the calcium sulphate should be precipitated not as dihydrate but as hemi-hydrate. Hence the influence of nitric acid in the treatment of phosphoric acid gypsum (dihydrate) was initially tested. Furthermore, the conditions were studied under which the dihydrate is converted into the hemi-hydrate.

The results of the study are shown in figure 1. As can be seen the dihydrate can be converted into the hemi-hydrate within a large range, in accordance with the nitric acid concentration and the temperature. The nitric acid concentration stated is that concentration which occurs after mixing the gypsum with nitric acid, i.e. the uncombined water content of the gypsum or hemi-hydrate, respectively, reduces the concentration of the nitric acid initially employed.

An interesting feature as regards the conversion of the calcium sulphate dihydrate into calcium sulphate hemi-hydrate with the aid of nitric acid, consisted in the extremely favourable purification effect and the good filtrability of the hemi-hydrate produced.

Using gypsum from Kola phosphate the following results were, for instance achieved :

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ fed :	
total P_2O_5	1.26 %
water soluble P_2O_5	0.14 % (related to anhydrous CaSO_4)

If we treat this gypsum with nitric acid without conversion to hemi-hydrate, we obtain :

total P_2O_5	0.96 %
water soluble P_2O_5	0.08 %
$\text{NO}_3\text{-N}$	0.04 %

The gypsum treated with nitric acid was washed with water at a ratio of 1 : 1.

If, on the other hand, we treat the same gypsum with nitric acid under conditions in which the conversion to hemi-hydrate occurs, while washing the cake similarly with water, we arrive at the following results :

total P_2O_5	0.08 %
water soluble P_2O_5	0.01 %
$\text{NO}_3\text{-N}$	0.003 %

Similar results were obtained with gypsum produced from types of phosphates other than Kola phosphate. Another factor to be considered in this connection consists of the fact that even very dark products become almost white after reaction. Hence only a slight yellow sheen may sometimes remain.

With gypsum from Morocco phosphate we obtained the following values :
(in respect of anhydrous CaSO_4)

	Raw Material %	Purification effect without recrystallization %	with recrystallization %
H_2O , total	39.6	39.0	25.0
Crystal water	20.7	20.3	6.2
N, total	-	0.003	0.005
NH_3 -N	-	-	-
NO_3 -N	-	0.003	0.005
P_2O_5 , total	1.05	0.77	0.03
P_2O_5 , water soluble	0.30	0.06	0.01
Na_2O	0.55	not measured	0.25
F	0.49	not measured	0.08

With gypsum produced from pebble phosphate the following results were obtained :

H_2O , total	35.7	40.4	20.6
Crystal water	20.2	20.2	6.4
NO_3 -N	-	0.005	0.002
P_2O_5 , water soluble	0.18	0.04	0.01
P_2O_5 , total	0.90	0.72	0.01
Na_2O	0.18	not measured	0.11
F	0.21	not measured	0.03

In the light of the conclusions reached with recrystallisation of calcium sulphate dihydrate to calcium sulphate hemi-hydrate with the aid of nitric acid, the following two-stage process can be designed (see figure 2).

In the first stage, phosphoric acid is initially produced in accordance with the conventional calcium sulphate dihydrate process. The gypsum produced, which is washed out with part of the filter washing water from stage two, is then converted in a second reaction vessel to hemi-hydrate, using nitric acid. The nitric acid employed, which contains the impurities of the dihydrate, is used, together with the phosphoric acid produced in the first stage, for the production of compound fertilisers in accordance with the nitro-phosphate process, whereas the very pure calcium sulphate hemi-hydrate is further processed for other applications such as the production of calcined gypsum plaster.

Apart from the advantage of a high efficiency in respect of the P_2O_5 introduced together with the rock phosphate and the available pure calcium sulphate hemi-hydrate, the two-stage process has also certain disadvantages. These consist in the first place in an unfavourable water economy of the process. For, with the exception of the crystal water of the hemi-hydrate formed, the entire water of the dihydrate gypsum passes into the nitric acid thus diluting the latter. Furthermore, some of the washing water from the hemi-hydrate stage, albeit a small percentage, enters the nitric acid. This water must either be removed from the nitric acid itself or, in the course of the complete fertiliser process, by appropriate evaporation.

III. Technical production process

In the light of the above disadvantages of the two-stage process the question arose whether pure calcium sulphate hemi-hydrate might not be produced in a single stage when manufacturing phosphoric acid, in order to avoid the disadvantage of the process consisting of the unfavourable water economy. In the course of these studies we initially developed a one-stage process in which only nitric acid was used by way of reagent, the sulphate ions required for precipitation of the calcium sulphate being introduced in the form of ammonium ions. A flowsheet of this process is shown in Figure 3. With this process nitric acid, ammonium sulphate and rock phosphate are fed into a reaction vessel (single tank). The concentration of the acid mixture is so designed that the calcium sulphate is produced in the form of calcium sulphate hemi-hydrate. The required temperatures must at the same time be ensured. Under these conditions it takes only a short time for well formed calcium sulphate hemi-hydrate crystals to occur; these are partly monocrystals and partly polycrystals, the size of which is such that they can be very easily filtered off and, owing to their small surface, readily cleaned from impurities using only a small amount of water.

After filtration by means of a phosphoric acid filter, the calcium sulphate hemi-hydrate produced has a total water content of 20-25%. With a crystal water content of 6-6.5% this corresponds to an uncombined water content of less than 15-20%.

The nitric acid concentration reaching the reaction vessel will in general depend on the available nitric acid plants, the concentration of the nitric acid fed to the reactor being adjusted, by addition of washing water, to about 50% HNO_3 . If only 50% nitric acid is available, the entire filter washing water must not be fed to the reaction vessel but, possibly after evaporation, to the final acid produced, in order to maintain the conditions required for the production of calcium sulphate

hemi-hydrate. With higher nitric acid concentrations the filter washing water may again be fed to the reaction vessel partly or wholly. In this connection it has been found that with nitric acid concentrations of more than 65% the entire washing water can again be fed into the reaction vessel. We may assume that at least 400 l water is required for washing per t calcium sulphate hemi-hydrate with a total water content of 23%.

Following the above processes at Embesen we have been manufacturing phosphoric acid for 2½ years in a technical plant. After initial difficulties the plant now operates faultlessly. We had at our disposal 75% nitric acid and Kola phosphate. Our production amounted to app. 10 000 tonnes of P_2O_5 per annum. In the middle of 1973 the calcium sulphate hemi-hydrate produced had a.o. the following composition (cf. A). The values were related to anhydrous $CaSO_4$.

	A	B
H_2O , total	24.9%	40.2%
Crystal water	6.1%	20.4%
P_2O_5 , water soluble	0.03%	0.00%
P_2O_5 , total	0.31%	0.26%
NH_3-N	0.075%	0.002%
NO_3-N	0.042%	0.000%
Na_2O	0.09%	0.06%
F	0.10%	0.08%
Yield	app. 99%	

The relatively pure hemi-hydrate thus produced (column A) can be processed without further purification. Although it is possible to achieve an even purer product by recrystallisation to dihydrate (stirring with water) (cf. column B), the costs are in this case greater than the advantage, particularly since the small proportion of foreign substances still present can be either removed by addition of small quantities of lime (e.g. NH_4^+) or neutralised (e.g. H_3PO_4 , HF) and converted to insoluble compounds having no disadvantageous effects in the quantities entailed, such methods being economically more favourable.

The resultant phosphoric acid which contains ammonium nitrate was subsequently used, together with ordinary phosphoric acid and nitric acid as well as rock phosphate, for the production of compound fertilisers.

Whereas, apart from the very high quality of the calcium sulphate hemi-hydrate, the above ammonium sulphate-nitric acid process offers advantages also in connection with the yield, the water economy and the quality of the calcium sulphate, by comparison with other processes, it does have the disadvantage that without addition of further phosphoric acid no fertiliser with an N : P_2O_5 ratio of 1:1, i.e. conventional fertilisers, can be

produced. This means that, apart from the ammonium sulphate-nitric acid-phosphoric acid plant a second phosphoric acid plant must be operated in the normal way, in order to produce such fertilisers. Furthermore, the market as regards ammonium sulphate has changed. There is no longer an abundance of ammonium sulphate, although a certain amount is always bound to be produced.

In order to neutralize the disadvantages of the normal nitric acid-ammonium sulphate process, which have already been mentioned, we partly replaced the ammonium sulphate-nitric acid by sulphuric acid, i.e. we produce, as it were, in a single plant normal phosphoric acid of high concentration and phosphoric acid containing ammonium nitrate at the same time. In this respect we have reached a stage enabling the production of fertiliser with an N : P₂O₅ ratio of 1:1 by using the nitrogen containing phosphoric acid which had been produced. This process also offers advantages from the point of view of the water economy in the fertiliser plant, since the water content of the acid thus produced is smaller than that of a mixture of phosphoric acid produced in accordance with the dihydrate process and acid produced via ammonium sulphate-nitric acid. In addition, more washing water is available for washing the filter cake than with weak nitric acid, owing to the high concentration of the sulphuric acid. With this process the crystals formed from the hemi-hydrate are mainly monocrystals and there are fewer conglomerates. For this reason the process may be somewhat more sensitive to fluctuations in the reaction conditions. We therefore decided to use one or the other process according to the type of fertiliser produced and the water economy required for granulation.

The calcium sulphate produced in this process had a.o. the following composition :

H ₂ O, total	22.2%	
Crystal water	6.2%	
P ₂ O ₅ , total	0.46%)
P ₂ O ₅ , water soluble	0.04%) related to anhydrous
NO ₃ -N	0.04%) CaSO ₄
NH ₃ -N	0.06%)

Hence sulphuric acid can, with the aid of nitric acid, be replaced by ammonium sulphate within a wide range, when producing phosphoric acid.

In general, the process developed by us has the following advantages by comparison with the conventional phosphoric acid process :

1. Very simple process, single stage, single tank, hence low investment and operating costs.
2. Production of a very pure calcium sulphate hemi-hydrate, which is well suited for further processing in the construction and cement industry.

3. Very high yields as regards the P_2O_5 introduced with the phosphate. Only small nitrogen losses.
4. Favourable water economy.
5. Low corrosion, even with stainless steel 4571 with the following composition :

Cr	17.5%
Ni	11.5%
Mo	2.2%
Si	1.0%
Mn	2.0%
C	0.1%
6. No blocking of pipes by silicon fluorides.

A further advantage consists in the possibility of reconverting the plant without major reconstructions to the dihydrate-phosphoric acid process and in the low costs entailed by the conversion of an existing dihydrate-phosphoric acid plant to the process.

IV. Utilisation of the calcium sulphate produced

The calcium sulphate hemi-hydrate produced is suitable for a.o. the following applications :

1. Production of gypsum wall slabs

The calcium sulphate hemi-hydrate produced can be used for the production of gypsum wall slabs without further purification. However, since the setting times of the pure product are too high, accelerators must be added. Favourable setting times and high hardness values can be achieved with relatively low densities. With an addition of 160 g hemi-hydrate to 100 g water, for instance, breaking strengths of above 200 kg/cm^2 were achieved with a density of 1.19 g/cm^3 . With higher additions amounting to 240 g hemi-hydrate/100 ml water, hardness values in the region of 400 kg/cm^2 could be achieved; a density of 1.4.

2. Production of gypseous stones

By pressing the α -hemi-hydrate produced it is possible to manufacture gypseous stones. After pressing the calcium sulphate is already so solid that no additions are required. Stones produced by ourselves exhibited breaking strength values of 450 kg/cm^2 with a density of 1.38 g/cm^3 .

3. Suitability of the material for the cement industry

The α -hemi-hydrate produced is mixed with calcium hydroxide. After 1-2 days over 90% of the material has been converted to dihydrate; in the course of this process any ammonia present escapes. After setting the virtually dry material can be sold direct to the cement industry.

4. Utilisation of the material for the production of gypsum plaster

Gypsum plaster can be produced by calcining material converted into dihydrate in accordance with 3.

V. Summary

It has been shown that it is possible to produce, by means of nitric acid, in a single-stage phosphoric acid process calcium sulphate hemi-hydrate which is so pure that it can be used in the construction industry without further purification.

This process is very economical, particularly if cheap ammonium sulphate is available.

C A P T I O N S

Figure 1 : Modification of calcium sulphate using HNO_3

- a. Range : $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
- b. Instable range
- c. HNO_3 concentration

Figure 2 : Production of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

Flow diagram : two-stage process

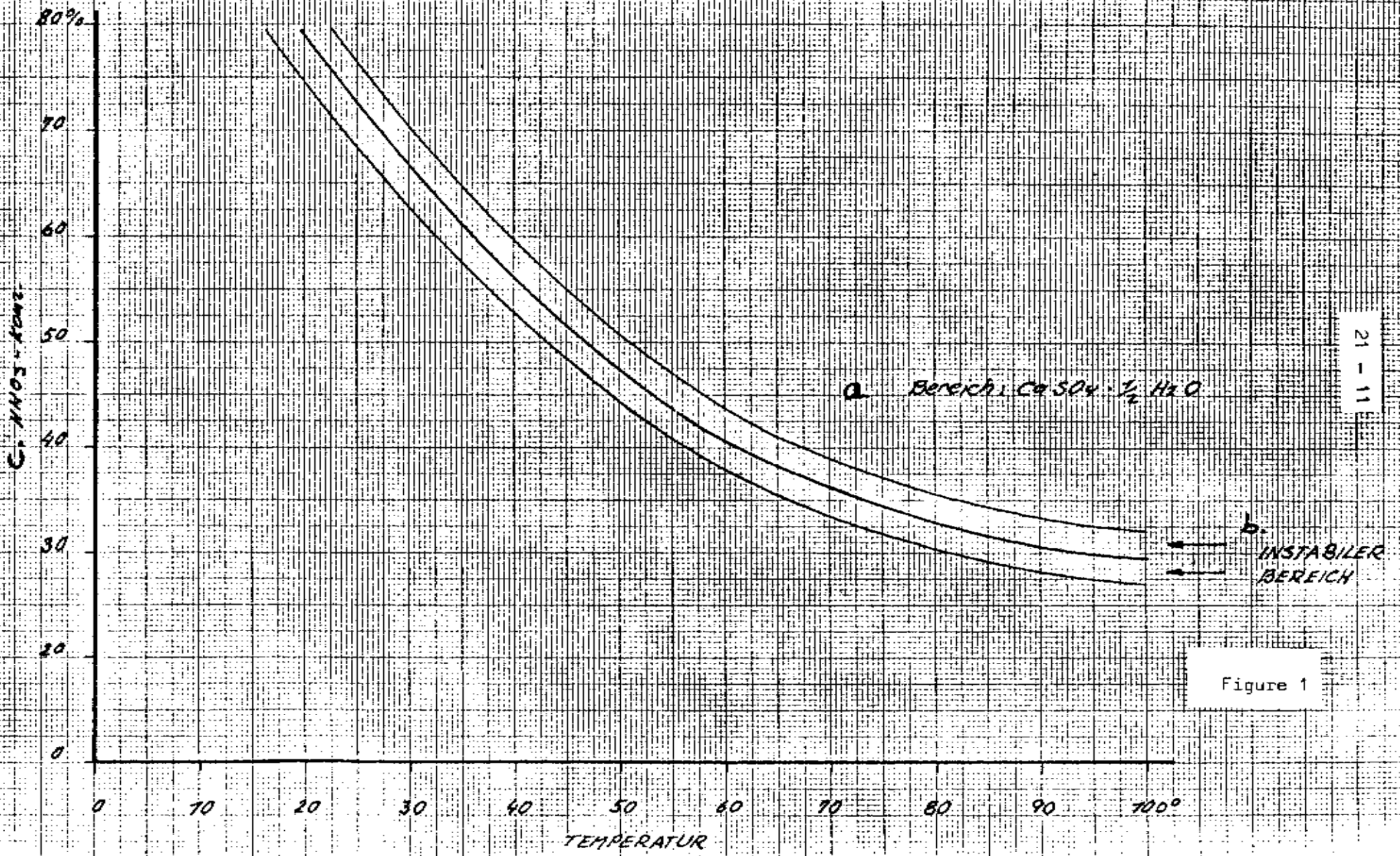
- a. 286 parts H_2SO_4 96%
- b. Recycle acid
- c. Reactor I
Decomposition
- d. 634 t $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with ab. 30% adherent water
- e. Recycle acid
- f. Reactor II
Hemi-Hydrate
- g. app. 335 t phosphoric acid containing app. 30% $\text{P}_2\text{O}_5/\text{HNO}_3$
- h. app. 865 t HNO_3 containing 47.5% phosphoric acid
- i. 433 t $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ with 20% adherent water = 345 t $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
- j. 1000 parts complex fertiliser 20-20-0

Figure 3 : Production of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

Flow diagram : single-stage process

- a. Rock phosphate
- b. Ammonium sulphate-sulphuric acid
- c. Nitric acid
- d. Recycle acid
- e. Washing water
- f. $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ with 20% adherent water
- g. Final acid consisting of : Phosphoric acid, Nitric acid, Ammonium nitrate,
water

Modifikationen von Calciumsulfat unter Verwendung von HNO_3



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Figure 1

HERSTELLUNG VON $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

Fließschema: 2-stufiges Verfahren

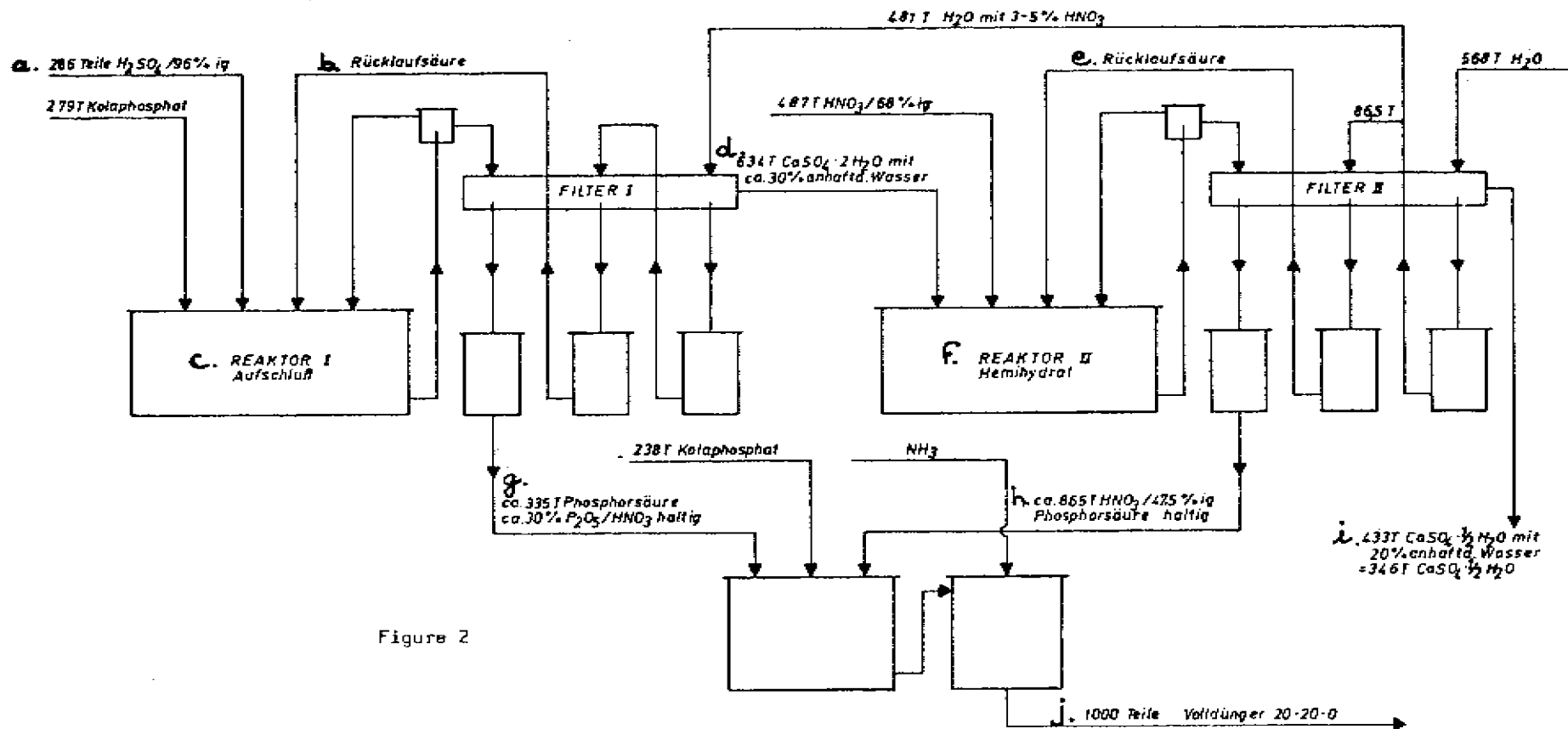


Figure 2

HERSTELLUNG VON $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

Fließschema: 1-stufiges Verfahren

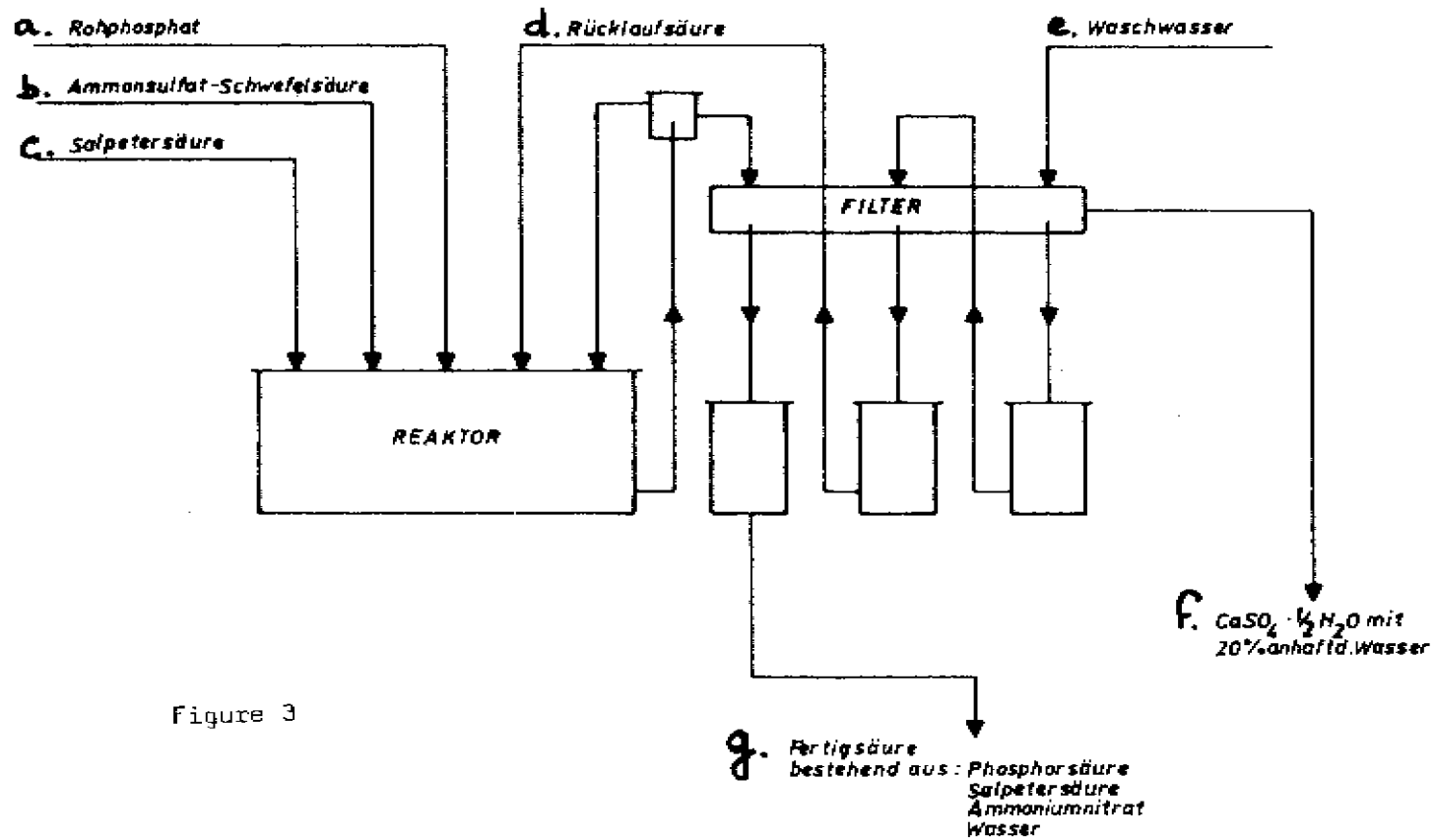


Figure 3

DISCUSSION

Dr KURANDI - (Vebe Chemie G.F.R.)

Our paper describes two processes for producing pure calcium sulphate hemi-hydrate: first a two stage process in which impure dihydrate obtained during normal phosphoric acid production is converted to hemi-hydrate by means of nitric acid. This treatment results in a very pure product, for which the quality of gypsum before purification plays a negligible role, e.g. that there is very little impure gypsum. The nitric acid used for the treatment, which contains the gypsum impurities, is used for the production of complex fertilisers by nitric reaction. In spite of the above advantages the two stage process has the disadvantage of an excessive humidity which remains in the nitric acid and must finally be removed during complex fertiliser manufacture.

For an economic operation, we developed a single stage process giving very pure calcium sulphate hemi-hydrate readily. The technique was developed by VEBA Chemie in Embsen.

In principle this process goes along with a phosphoric acid process in which more or less sulphuric acid replaces ammonium sulphate. Thus nitric acid must fill the following duties :

- 1/ It achieves the complete reaction of phosphate rock.
- 2/ Sulphuric acid can be replaced by ammonium sulphate, since nitric acid supplies the acidity needed for phosphate rock reaction.
- 3/ For reaction temperatures of 70-90°, the α hemi-hydrate is stable in the reaction.
- 4/ Hemi-hydrate crystal growth is enhanced, which means a smaller reactive volume and no recycling necessary.
- 5/ The viscosity of the solution is decreased so that the efficiency of the filter is improved.
- 6/ Nitric acid dilution results in a lower P_2O_5 content of the slurry which, beside other reasons, contains pure calcium sulphate.

The process operates as follows :

Slide 1 - The necessary ingredients, rock phosphate, sulphuric acid, nitric acid and ammonium are fed in a single reaction tank. The precipitation of calcium sulphate hemi-hydrate takes place at reaction temperatures of 70 - 90° C. The α hemi-hydrate precipitated is easily filterable (slide 2). The filtration is achieved in a Giorgini filter (slides 3 and 4). The production of α hemi-hydrate of 60 t/d. P_2O_5 can be filtered and washed in two stages. To precipitate calcium ions, sulphate can be used in the form of ammonium sulphate as well as sulphuric acid, so that the respective amounts of these two ingredients can vary greatly. In the production plant we first used ammonium sulphate with nitric acid as a reaction material. With this nitric acid-ammonium sulphate mixture we could replace up to 75 % of the sulphuric acid. Phosphoric acid produced in this process and containing nitrogen is used to make complex fertilisers by the nitrophosphate process. Formulations with N : P 1 : 1 ratios can also be made. The advantage of this process is the high purity of the α hemi-hydrate and in a very great efficiency of the process.

In terms of the P_2O_5 fed the losses are lower than 1 %. Ammonium sulphate and nitric acid losses are remarkably low (slide 5). Another advantage is the possibility to shift from sulphuric acid to ammonium sulphate.

The α hemi-hydrate produced has multipurpose uses as construction material (slide 6). After removal from the filter it is mixed with lime in a pugmill (slide 7). After a setting time of at least two days the remaining material is used as a cement material according to Knauf process in which the normal purification and first calcination stages of the Knauf process are no longer necessary when using our product which makes the production of plaster gypsum highly profitable.

DISCUSSION OF PAPERS N° 18, 20, 21Monsieur KREMPF (Cerphos, France)

The treatment of calcium sulphate resulting from the manufacture of phosphoric acid has for many years been the subject of concern for technicians, and the purely economic aspect of the question has recently been made more complicated by pollution problems. At first glance, it is indeed surprising to realise that sulphur in the form of SO_4 does only pass through phosphoric acid plants to be finally totally discharged as a by-product. Hence, the most logical idea, although thermodynamically difficult to implement, of recycling SO_4 in the form of H_2SO_4 by extracting it from gypsum while the Ca is itself used in the cement.

A more simple treatment of phospho-gypsum, which has the additional advantage of relieving its economics from the variations of the price of sulphur, is the use of phospho-gypsum as raw material for plaster. Already the amounts of chemical gypsum available would be sufficient to substitute entirely for the natural gypsum from quarries. It is thus hoped that not only the problem of pollution by phospho-gypsum would partly be solved, but also that the deterioration of nature in certain areas due to the mining of natural gypsum quarries could be avoided. It should be remembered that 1000 t.p.d. P_2O_5 phosphoric acid plants, currently erected in the world, discharge more than 5000 t.p.d. of phospho-gypsum, that is more than 1.5 m.t. p.a.

In these 2 processes for using phospho-gypsum - H_2SO_4 and plaster manufacture - the impurities of the raw materials still exist.

- 1 - The Chemie Linz Company successfully overcame the difficulties arising from the use of phospho-gypsum in the manufacture of H_2SO_4 and cement, as Mr Binder showed in his paper how for more than 5 years large amounts of sulphuric acid have been manufactured by his company and its licensees from phospho-gypsum.

Although the economic problem resulting from the co-existence of 3 plants might be complex, I would like to ask Mr Binder the order of magnitude of the cost of the purification of phospho-gypsum - reduction of water, P_2O_5 and F contents - or if you prefer the equivalent of natural anhydrite, giving the same cost of H_2SO_4 including the last improvements relating to the thermal exchange which C.L. company made in the process.

In addition, is there a corrosion problem, of the gas purification section in particular, due to the fluorine which would increase the investment ?

- 2 - Regarding the purification of phospho-gypsum to make plaster, Mr Kurandt from Vebe Chemie gives an original idea on the use of calcium sulphate resulting from a sulphuric nitric reaction. By studying the balance system hemi-hydrate-dihydrate in a nitric solution, Mr Kurandt obtains a hemi-

hydrate containing very little impurity and perfectly adequate for use in the construction industry. I would like to ask the author a few questions about the filtration of hemi-hydrate obtained in his plant : What is the influence of $\text{HNO}_3/\text{H}_2\text{SO}_4$ on the crystallisation of hemi-hydrate and what is the filtration rate in the plant ? In addition, does the presence of nitric acid not change the kinetics of crystallisation which might result in possible transformation on the filter or in idle parts of the circuit ? Finally, the results given by Mr Kurandt relate to Kola phosphates which, as we heard this morning, are characterised by a low crystallisation rate. Have you tested other rocks ?

- 3 - Giulini Company is known by all specialists as one of the pioneers of the technique of using phospho-gypsum in conventional phosphoric acid plants. The use of the crystallisation of phospho-gypsum in an autoclave enables Giulini to obtain high performance "Alpha" plaster. I would like to ask Dr Forster two questions: The first relates to the variation of the properties of plaster according to the shape of the crystals: in his paper Dr Forster recommends the use of additives specific to the shape and size which he would like to give the crystals. What are the practical criteria used for this choice and is it possible to achieve all the shapes desired whatever the original gypsum? The second relates to the recycling of the autoclave liquors. Do these liquors contain impurities other than P_2O_5 and, if so, would crystallisation of phospho-gypsum in reaction tanks not be disturbed by them ?

Dr BINELLA (Chemie Linz), Austria)

To estimate the profitability of the gypsum/sulphuric acid process using phospho-gypsum, we did not attempt to evaluate the cost of each stage of the process such as drying, fluorine removal etc..... It is possible to make an actual comparison of the profitability by comparing the production costs of sulphuric acid made from sulphur and from phospho-gypsum, making allowance for the credit represented by cement. In very special cases only a more precise comparison can be made for each factor, case by case, as the cost of raw materials and energy, the water and fluorine removal from phospho-gypsum. To give you an idea I have compared the production costs of a 1000 t.p.d. sulphuric acid plant from sulphur and the same from phospho-gypsum in the conditions prevailing at that time in Austria. We started from humid phospho-gypsum. Drying and fluorine removal were included in the comparison. Assuming that the cost of disposing of phospho-gypsum in heaps was about \$1.5 p.t., the production costs for sulphuric acid are the same for both processes. In Austria, for example, it is no longer allowed to dispose of phospho-gypsum. During calcination, there are naturally corrosion problems. However, we have found special steel which is remarkably resistant to corrosion.

Dr FORSTER

Question 1. We play on the shape of crystals, the temperature, the pH, the feedrate etc...

Question 2. Yes, in the laboratory in a pilot plant and on a commercial scale, we have made about 200 tests on phosphates from the whole world.

Question 3. This depends obviously on the gypsum used. We can quote the following contents : (see figure on the paper).

Research carried out so far jointly with other phosphoric acid producers showed that, when the phosphoric acid reaction slurry is recycled, there is no detrimental influence.

Dr KURANDT

1. By supplying an increasing amount of nitric acid, it means increasing what you call the $\text{HNO}_3/\text{H}_2\text{SO}_4$ ratio, the crystals resulting from the agglomeration of individual crystals no longer form, but, instead, mainly well constituted individual crystals. The filtration rate is only slightly reduced, I would say by about 10%.

2. In that production plant production is about 60t.p.d. P_2O_5 with a 9m^2 filter.

3. The difficulties arising from tube clogging and from the crystalline transformation of hemi-hydrate into dihydrate have frequently been studied by ourselves in the course of production.

4. In our plant we use only Kola phosphate. It is the optimum material to be treated in the process. We used other phosphates only in the laboratory and we found that the filtration rate can be reduced.

Mr JEMAA (SIAPE, Tunisia)

I would like to emphasize the fact that, because of their chemical composition, some phosphates contain substantial amounts of alkaline salts and the processed water can also contain some sodium chloride. In that case, the fluorine balance in the phosphoric acid plant is completely altered insofar as nearly 60%, and even more, of the fluorine in the phosphate can be discharged in the phospho-gypsum. Two processes are presented here, from Giullini, and from Chemie Linz. The first seems radical since it solves the problem directly by recrystallising the phospho-gypsum produced and hence removes the P_2O_5 and fluorine in the form of silicofluoride. In that case one could imagine an integrated complex where both processes could be used. The Giullini process would produce plaster and supply a purified phospho-gypsum to the Chemie Linz process. I would like to ask Mr FORSTER if it is possible for him to give us an idea of the investment and the operational conditions such as those which Dr RICHTER described concerning aluminium trifluoride. To Mr BINDER I would say that this powder is a nuisance to us.

In the Arab world we have a fairly favourable position from an energy viewpoint. Did VOEST carry out tests with natural gas to make sulphuric acid and cement ?

Dr FORSTER

Regarding the investment costs, I would like to give figures which I have in mind but which I have not checked. For a 200 t.p.d. plant, without storage or premises, the order of magnitude is of 8-9 million DM. Regarding the operational costs, I can tell you that the value for plants with a capacity of 300-600 t.p.d. "Alpha" hemi-hydrate are about equal to those for natural gypsum, that is 25-300 p.t.

Dr BINDER

In the process it is possible to use natural gas for operating the rotary kiln and for drying the gypsum. Concerning the reduction of calcium sulphate, only coke or another product derived from coal can be used. The consumption is however fairly low, about 100 kg p.t. sulphuric acid and cement clinker.

Mr JENSEN (Superfos, Denmark).

When you use the water from the gypsum plant for washing the phosphoric acid filter you will be washing with a water containing P_2O_5 and fluorine. Therefore your washing will be less effective than washing with pure water and you will get a gypsum back to the purification plant with a higher content of P_2O_5 and fluorine than when you started.

This means that the water now coming from the gypsum plant will have an even higher content of P_2O_5 and fluorine and you are in some sort of a bad circle. Where do you end and how do you get out of the circle again?

Perhaps you can use some of the water for dilution of the sulfuric acid, but this amount of water is small compared to the amount of water which you are using on the filter.

Dr FORSTER

The projects we have surveyed and commissioned, or about to be, are designed in such way that the whole precipitated gypsum is passed at the same time. The result is that, after precipitation in the slurry, the amount is such that the dilution of water of sulphuric acid can be replaced.

Dr NEUMANN (Davy Power Gas GmbH, Germany)

I would like to ask a question about Dr BINDER's Table 2 regarding the constitution of by-product gypsum from phosphoric acid produced from Kola phosphate, which shows a high fluorine level of 1.7 %. If I remember well, with Kola phosphate you obtain a fairly low F content in the gypsum. My question is: so far, about 350,000 tons of gypsum have been treated. The maximum permitted fluorine content is 0.15%. Did you test a method for removing

fluorine from phospho-gypsum containing too much F or did the gypsum used initially fulfill these conditions? My question also relates to this : There are essentially two possibilities of reducing the F content from the maximum you have mentioned: first of all, the choice of the phosphoric acid process can, according to process conditions, give a gypsum containing little F. It is also possible to reduce the F content through existing techniques. Did you consider the problem? Which method would you recommend in the future : either the use of a phosphoric acid process avoiding directly this high F level, or a treatment after reaction?

Dr FORSTER

Regarding your question on the analysis of gypsum obtained from Kola phosphate given in Table 2, it relates to a plant where active silica and sodium sulphate were fed in, resulting in a high F content of the gypsum.

Dr BINDER

In our plant we treat gypsum obtained from Kola phosphate and as you said the F content is within the tolerance limit, at any rate not higher than 0.15 %. As you rightly suggested, obviously the F content of the slurry can be reduced. There are two alternatives. If it is possible to modify a phosphoric acid plant, we would obviously choose a process which would remove F from the gypsum in the plant. On the other hand, when it is not possible to do so, the fluorine content of the slurry must be greatly reduced.

Dr W. JANICZEK (Fertilizer Institute, Poland).

I would like to ask a question about paper n° 18. In which kind of construction material the Portland cement produced by your process can be used ?

Dr BINDER

The Portland cement which we produce is controlled by the Standardisation Commission in the same way as the Portland cement obtained in normal cement works and can be used in any kind of construction.

Dr. H. RESSEL (Farbwerke Hoechst - Werk Knapsack - Germany)

Dr FORSTER said that the conversion of dihydrate into "Alpha" hemi-hydrate occurs in the soluble phase. Is it not only partial since there certainly is a topochemical reaction and that some metamorphosed dihydrate is to be found in hemi-hydrate crystals so that the reaction does not take place in the soluble phase?

Dr FORSTER

You are right Dr RESSEL. There are cases in which the conversion takes place in a topochemical way. This is also true.

Mr MORAILLON (Générale des Engrais, France)

I would like to ask Dr KURANDT firstly regarding the construction material of the reaction tank, as far as I know initially this tank was of concrete lined with rubber or carbon bricks. I do not believe these materials can be used when nitric acid is introduced. Can you confirm this point? Secondly, do you intend to do away completely with ammonium sulphate in your process? Thirdly, I did not understand if you used directly hemi-hydrate without rehydration or if you let it rehydrate outside. However, it seems to me that in that case, the calory consumption is increased and that it would be preferable to use it directly.

Mr KURANDT

Regarding the reactor we use a normal phosphoric acid reactor made of steel lined with rubber and carbon bricks and we converted this reactor for the "Alpha" hemi-hydrate process by using refined steel.

The second question referred to ammonium sulphate. Initially, ammonium sulphate was very cheap and could be used very economically, more so than sulphuric acid plus ammonia. Since then, conditions have changed, and ammonium sulphate is more expensive. However, this depends on the source available. If ammonium sulphate is cheaper than sulphuric acid plus ammonia, it is normal to use it. On the other hand sulphuric acid can be used and, as I mentioned, we have fed up to 75% sulphuric acid. If ammonium sulphate was to become more expensive, to feed more sulphuric acid the plant would have to be modified, which would involve heavier investments in view of the more important reaction which takes place. At present, these additional investments are not necessary as ammonium sulphate is not yet more expensive than sulphuric acid plus ammonia.

Regarding the third question, which refers to the direct introduction of "Alpha" hemi-hydrate, of course it is preferable to introduce that material directly. We have studied this problem with Knäuf Company and, as gypsum experts, they believe that there is still a crystalline conversion before the last scrubbing, so that it is preferable first to have the crystalline conversion and then to calcine. The moisture is the same whether the conversion takes place or not. Unfortunately, it is true that hydration should take place before, which means that heat must be removed when hemi-hydrate is converted into dihydrate, and there are additional intermediate storage costs. However, this additional cost should make it possible in the future to introduce "Alpha" hemi-hydrate.