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

FLUORINE EMISSION CONTROL OF THE NEW UKF-NPK PLANT AT
PERNIS - THE NETHERLANDS

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SUMMARY

At the UKF-site in Pernis a new NPK-plant was started up in mid 1978. This plant, replacing three old units, has a capacity of 330,000 tons/year. The essential parts of the new plant consist of an ammoniator-granulator with a pipe reactor, a dryer and a cooler. NH_3 containing off-gases are scrubbed with phosphoric acid.

During the start up of the plant the operators were confronted with a higher than expected fluorine emission from the acid scrubbing system, occasionally with a heavy mist formation. Often the F-emission went up to more than 20 kg/h, exceeding by far the 1 kg/h allowed by the authorities.

Analysis revealed this mist to consist mainly of $(\text{NH}_4)_2\text{SiF}_6$, which could easily be confirmed in laboratory experiments. From practical figures it was known that fluorine emission decreases at higher N/P mole ratios in the scrubbing liquid. Investigations on lab scale showed that already at mole ratios higher than 0.3 mist formation stopped almost completely and F-emissions decreased to less than 0.5 kg/h.

Based on these results the acid scrubbing system in the plant was rearranged. The scrubbing liquid is maintained at an acid strength of 40% m/m P_2O_5 and a N/P mole ratio of approx. 0.5. Instead of an F-emission of 10 kg/h, with peaks of more than 20 kg/h, the emission is now reduced to an invisible plume with less than 1 kg/h of F and mostly in the order of 0.2 - 0.3 kg/h of F.

By investigating the scrubbing liquid a new crystalline compound was discovered with an overall composition $8(\text{NH}_4)_2\text{SiF}_6 \cdot \text{K}_2\text{SiF}_6$.

The application of the new scrubbing system obviated the use of sulphuric acid. The plant flexibility is maintained, and since no sulphate results in the end product, the quality is good. On the basis of previous plant experience sulphate is a significant cause for deterioration in product quality due to increased plasticity.

INTRODUCTION

At the UKF-site in Pernis a new NPK-plant was started up in mid 1978. It has a capacity of 330,000 tons/year, 1000 ton/day.

The plant was designed by a UKF-workgroup, and it is a very flexible plant. Quite a large range of fertilizers can be produced, some of them as components for bulkblends.

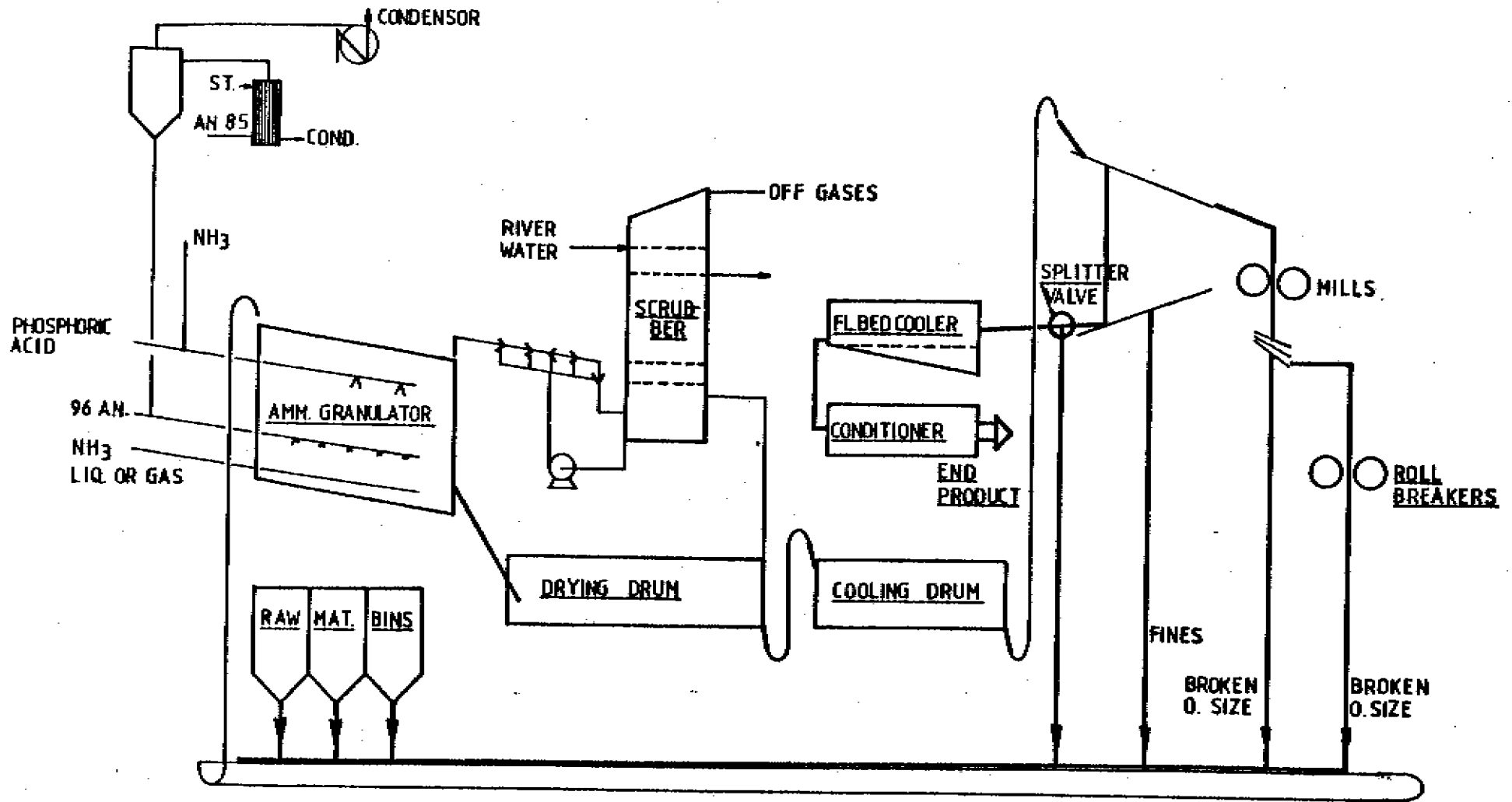


Fig. 1. - Flow diagram NPK-granulation plant UKF-Pernis.

The following fertilisers have been produced up til now:

11 - 11 - 33	17 - 17 - 17
14 - 28 - 14	12 - 10 - 18
15 - 12 - 24	15 - 11 - 22

Most of these are high grade complex fertilisers, and so it is important to have quite pure feedstocks. Sometimes single super phosphate is used as filler.

The plant has a great flexibility because of the different ways of feeding the nutrients to the granulation unit. Ammonium nitrate is obtainable in concentrations of 85 to 96%; ammonium phosphate can be made by a pipe reactor and by direct ammoniation in the ammoniator-granulator. All kinds of concentrations of phosphoric acid and N/P mole ratios can be reached. In the ammoniator liquid or gaseous ammonia can be introduced.

During start-up it was difficult to establish the proper granulation conditions to produce the different kinds of fertilisers.

In addition we encountered high fluorine emissions. The permitted F-emission is 1 kg/hour in 100,000 m³ off-gases. The measured emission was 20 - 30 kg/hour as fumes, which couldn't be caught by the scrubbing systems. It took three months to get out off these problems but the results were very interesting.

DESCRIPTION OF THE PLANT

The heart of the NPK-plant is the ammoniator-granulator; it is a 8 x 4 meter granulation drum. (See figure 1).

The solid materials - raw materials and recycle stream - are fed to the drum by an elevator.

The fluid materials are introduced in three ways:

1. AN melt by a spray pipe over 60% of the length of the drum;
2. Ammonium phosphate melt is sprayed by two pipe-reactors. Each reactor has two nozzles;
3. Ammonia, liquid or gaseous, is added to the bed by a sparger.

In the ammoniator the solid and fluid materials are mixed and react with each other. The so-formed granulate is dried in a drying drum.

The off-gases from the granulator and the drying drum are cleaned by a scrubbing system. Phosphoric acid is sprayed in the ducts after the ammoniator. The gases after the drying drum pass a set of cyclones and are cleaned in the scrubber. The scrubber was equiped with 3 impingement plates for ammonia scrubbing, and 2 impingement plates for fluorine scrubbing.

The granulate is transported by an elevator from the drying drum to a cooling drum. This cooling drum is necessary for cooling the granulate when a too high temperature in the granulation drum occurs resulting in over-granulation. After this drum the granulate is screened and the oversize crushed. The undersize from the screens and the crushed oversize together with the raw materials are transported by a

recycle belt to the granulator-ammoniator. The end product is cooled after the screens by a fluidised-bed cooler and after conditioning, the product is transported to the storage.

An important point is that for the UKF-site at Pernis the use of the following equipment was on innovation:

1. pipe reactor
2. granulate cooling drum
3. AN-concentrator

1. The pipe reactor used in the NPK-plant is of our own design. UKF spent 2 years' research to develop a new concept of the T.V.A. pipe reactor. The new concept was necessary because of the need of making diammonium phosphate. With the TVA pipe reactor this is not practicable even with two-stage ammoniation. The UKF pipe reactor can produce a slurry with N/P mole ratio of 1.4. With this slurry it is easy to ammoniate further in the drum to N/P ratio of 1.8. Different concentrations of phosphoric acid can be used for the pipe reactor, from 35 to 50% P₂O₅-depending on the water content necessary for optimal granulation. The N/P mole ratio can be altered between 0 to 1.4 depending on the required mole ratio in the end product, and the temperature or quantity of fluid phase in the granulator drum.

2. The granulate intermediate cooling drum installed in the plant gives an extra degree of freedom in granulation control. In the case of over granulation the granulate can be cooled to decrease the mean particle size, instead of operating at a higher recycle ratio. When a product like 14 - 28 - 14 is made, with a high content of AN and P₂O₅, the heat content is very high, so cooling of the granulate is advantageous to avoid over granulation. The cooling drum gives a facility to change the granulation to its optimum.

3. The ammoniumnitrate concentrator is a vertical one-pass evaporator of Stamicarbon design. AN is concentrated from 85 to 96% under vacuum.

With the concentrator it is also possible to heat the solution when only sensible heat and not a highly concentrated solution is necessary for the granulation. The concentrator condenser is cooled by air. The warm air from this condenser is used as secondary air for the burner of the drying drum.

OPERATION OF THE PLANT

Due to the great number of operating variables it was very difficult to determine the correct operating conditions in the start-up phase of the plant. Particularly in the competitive market conditions of Western-Europe the quality of the product should be as high as possible.

Nowadays these variables are well established and the quality of the end product is acceptable. By controlling the granulation temperature and moisture content in the ammoniator-granulator the recycle ratio can be kept low.

The pipe reactor produces a slurry with a N/P ratio of 1.3, with a feed concentration of the acid of 45 - 47% P₂O₅. Usually the AN concentrator operates at a concentration of 96%. Operation of the pipe reactor is easy, the N/P ratio is kept constant by a ratio controller. Starting and stopping of the pipe reactor occurs by starting and stopping the feed pumps. This is much easier than a preneutraliser process where a by-pass stream is necessary. To increase the mole ratio liquid or gaseous NH₃ is introduced in the bed by a sparger. To achieve a higher granulation temperature gaseous ammonia is used.

The design is based on a combination of the ICI Sherrington and UKF-van der Leek theories*). Sherrington emphasizes the solid/fluid phase ratio in the granulator and van der Leek the interaction of the screening and crushing units with the working of the granulator. However, the solid/fluid phase ratio must be kept constant in the granulator to get a constant mean particle size of the end product. Therefore a splitter valve in the good product stream, after the screens, sends product back to the granulator (via the crushers) to stabilise the recycle stream. The recycle/feed ratio is held between 2.5 and 3. With this low ratio and the high granulation temperature, the use of natural gas is low: 0.5 m³/ton product. Due to the low moisture content of the granulate, the plant stays clean, even the mills and screens.

SCRUBBER PERFORMANCE

One of the major problems encountered during start-up of the plant was the high F-emission of the scrubber. The scrubber is equipped with impingement trays. Phosphoric acid from the Nissan-plant is circulated over the trays. During this circulation of the acid F is emitted from the acid. Table 1 gives exit-gas analysis from the period September to December 1978. The permitted upper limit for F-emission is 1 kg/h. As can be seen from table 1 this value was exceeded all the time. When this high emissions coincided with unfavourable weather conditions mist formation gave severe problems with the navigation on the river to the important harbour of Rotterdam. Heavy penalties could be envisaged if no sound solution to this problem was to be found. With new plants the government considers the application of the limits very seriously, so our company was forced to improve the scrubber performance as a matter of urgency.

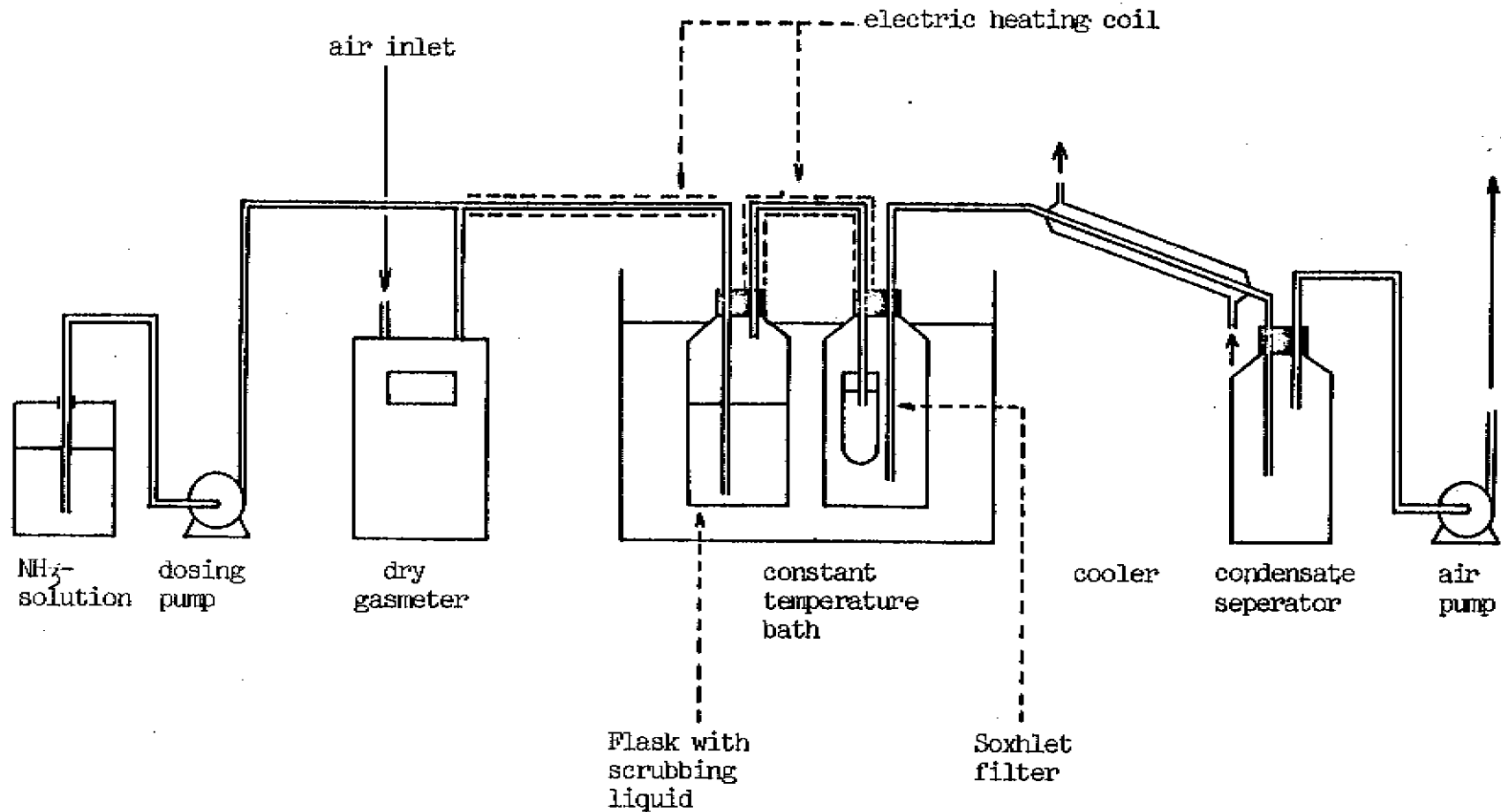
Little literature exists about this subject, one thing known was the fact that in the DAP-plant at our site the F-emission is lower with DAP-production than with MAP-production. The principal difference was the N/P mole ratio in the scrubber liquid. Also in our NPK-plant in England which works with high N/P mole ratios in the scrubbers, no significant F-emission was measurable. This was the starting point to investigate the problem in more detail on laboratory scale.

*) ISMA-Technical Conference, The Hague, 1976.

Tabel 1.: Emission figures (kg/h) of effluent gasstream before application of the split-feed system (September - December 1978).

Date	F	NH ₃	SiO ₂	Cl	off-gas m ³ /h	Product
13- 9-'78	2,17	5,35	8,07	8,53	75.000	15+20+20
15- 9-'78	7,98	0	17,56	0	90.000	15+20+20
11-10-'78	7,7	0	3,09	0	103.000	15+12+24
12-10-'78	13,17	0,5	4,85	0	100.000	15+12+24
24-10-'78	6,56	1,67	3,41	0,19	92.000	15+15+15
10-11-'78	21,7	6,1	9,75	0,86	99.000	14+28+14
1-12-'78	13,1	7,3	6,0	-	-	15+15+15
5-12-'78	23,8	7,76	12,3	-	-	15+12+24

Fig. 2
Experimental apparatus for measurement of mist-formation in acid scrubbing of NH_3 -containing air with HF and H_2SiF_6 containing phosphoric acid.



RESEARCH ON MIST FORMATION

Looking to the mist formation it was soon realised that the well-designed scrubber couldn't do the job it was meant to do, as long as mist formation jeopardizes good absorption of ammonia. Mist formation must have something to do with a gas phase reaction between ammonia and gaseous fluorine compounds (HF en SiF_4) evolving from the acid.

Fortunately in the preceding period our Centraal Research Laboratory did measurements on the partial HF and SiF_4 -vapour pressures above phosphoric acid at different concentrations and temperatures in connection with a study to improve our phosphoric acid concentration plant. From this study we could determine that the concentrated phosphoric acid used as scrubbing liquid still has a not insignificant HF and SiF_4 -vapour pressure.

On another occasion when analysing acid-mist from triple-super production we found that this mist could easily be caught by passing the gas through a soxhlet-filter. This method was also used to catch the mist particles in this case, and proved to be very succesful. The crystalline compound we found in the filter proved by X-ray and chemical analysis to be mainly $(\text{NH}_4)_2\text{SiF}_6$, ammonium silico fluoride. Some NH_4Cl also appeared in the samples when fine dust particles from the product dryer passed through the cyclones to the scrubber in the production of KCl -containing fertilisers.

In order to study the phenomenon in more detail a laboratory experiment was set-up to reproduce this mist formation under well defined conditions. Figure 2 gives an outline of the experimental set-up. Diluted NH_3 -solution is sprayed into a N_2 -gas stream in such a way that an NH_3 -concentration of 1000 or 2000 mg/m^3 is maintained, together with a water vapour pressure comparable with the actual pH_2O in the plant gas stream. From this gas stream 500 dm^3 is washed with approx. 400 - 450 g phosphoric acid at different strengths, temperatures and N/P mole ratios to investigate the parameters influencing F-emission and mist formation. Two sets of concentrations and temperatures were chosen: approx. 50% m/m P_2O_5 and 80°C , corresponding with the use of concentrated acid with some dilution, and approx. 32% m/m P_2O_5 and 50°C , corresponding with the use of weak acid. The chosen temperatures correspond with those calculated and also found in practice at thermodynamic equilibrium. First the N/P mole ratio was chosen so that no monoammonium phosphate crystals could be expected. The experiments were so designed that we might expect an almost proportional decrease of the F-emission as a function of the degree of neutralisation. The immediately visible result: the complete disappearance of the mist at a N/P mole ratio above 0.3 however surpassed the expectations.

In table 2 the complete results of this series of measurements are compiled. It is clear that a strong interaction exists between $(\text{NH}_4)_2\text{SiF}_6$ -mist formation and N/P mole ratio in the scrubbing liquid and the P_2O_5 -concentration. Neutralisation to a N/P mole ratio higher than 0.3 in combination with a lower

Tabel 2: F-emission measurement on ammoniated phosphoric acid

Gas composition: 1000 mg/m³ NH₃-N

composition scrubbing liquid										°C	mist x) (mg) in Soxhlet	condensate w%		
N/P mole ratio		w% P ₂ O ₅		w% F		w% SiO ₂		w% NH ₃				F	SiO ₂	NH ₃ -N
before	after	before	after	before	after	before	after	before	after					
.01	.02	49.8	50.3	.62	.36	.19	.07	.06	.15	80	602	1.26	.78	.0037
.16	.17	49.2	49.7	.62	.54	.18	.16	1.55	1.71		151	.51	.29	.0014
.30	.31	48.0	51.3	.55	.55	.16	.14	2.87	3.17		22	.20	.10	.0010
.56	.58	46.0	50.0	.58	.62	.19	.21	5.04	5.70		3	.05	.02	.0009
.01	.03	33.1	33.4	.42	.42	.13	.14	.04	.17	50	4	.04	.018	.0014
.16	.18	32.6	33.7	.42	.42	.12	.12	1.04	1.19		2	.02	.010	.0025
.30	.31	33.0	33.6	.42	.42	.13	.14	1.98	2.04		2	.01	.006	.0033
.58	.59	34.4	34.3	.39	.38	.11	.12	3.91	3.99		1	.01	.005	.0039
.01	.03	32.4	32.4	1.31	1.33	.61	.62	.05	.17	50	2	.044	.008	.0160
.16	.18	32.2	32.9	1.31	1.30	.61	.61	1.01	1.14		6	.020	.006	.0050
.31	.33	32.3	33.0	1.29	1.27	.59	.60	1.99	2.12		2	.014	.005	.0083
.47	.49	32.1	33.2	1.33	1.18	.61	.59	3.00	3.19		1	.008	.002	.0078
Gas composition. 2000 mg/m ³ NH ₃ -N														
.01	.04	32.4	32.8	1.31	1.32	.61	.61	.05	.27	50	50	.015	.002	.0120
.16	.19	32.2	33.0	1.31	1.32	.61	.61	1.01	1.22		8	.029	.007	.0115
.31	.34	32.3	33.1	1.29	1.29	.59	.59	1.99	2.22		5	.016	.006	.0075
.47	.50	32.1	33.5	1.33	1.22	.61	.58	3.00	3.31		2	.008	.003	.0070

x) Solid consists almost completely of (NH₄)₂SiF₆.

P₂O₅-concentration by mixing weak wet-process phosphoric acid with concentrated acid gave a F-emission far below the limits required by environmental regulations (see table 3).

On the basis of chemistry there was not immediately a complete explanation of the phenomenon of the decrease of the F-vapour pressure at a N/P mole ratio exceeding 0.3. In the literature several F-containing compounds are mentioned, such as NH₄(Fe,Al)F₂.HPO₄*). In experiments in neutralising wet phosphoric acid we also found precipitations with an empirical formula of approx. (NH₄)₂(Fe,Al)H₄(PO₄)₂F₃ containing approx. 15% F up to a pH of 4.5. Possibly the formation of the insoluble K,NH₄-silico fluoride mentioned further on in this paper plays an important role in the explanation of "de-activation" of the fluorine.

NEW SCRUBBER DESIGN

On the basis of laboratory results the scrubbing system ought to be rearranged. It was soon recognised that instead of passing the whole acid stream over the scrubber it is more sophisticated to split up this stream and to send only as much acid to the scrubber as is needed to absorb the NH₃ out of the scrubbed gas stream and to maintain the wanted N/P mole ratio in the scrubbing liquid. The scrubber has now been rearranged and runs on the basis of the following conditions:

1. Scrubbing of ammoniacal gases is done by recirculating acid with a N/P mole ratio higher than 0.35.
2. To avoid a too high concentration of the acid there is need for condensate addition in the scrubber.
3. The conditions of the scrubber liquid are given on fig. 3. Under ideal circumstances with a specific gravity of 1475 kg/m³ with a mole ratio of 0.4 of the scrubber liquid, the F-emission at an air through-put of 100,000 m³/h is 0.5 kg/h. With a higher specific gravity crystallisation occurs and with a lower mole ratio the F-emission becomes too high. The feed acid for the pipe reactors is made up by a mixture of the slip-stream from the scrubber and concentrated phosphoric acid. The so formed acid supply to the plant is called the split-feed system. In table 3 the results with this split-feed system are given. Comparison with table 1 for the situation before the alteration again make clear the big improvement achieved with this rather simple change. The system works perfectly and it gives no problems with the ammonia efficiency of the plant so all products can be made. The split feed system is also applied in the DAP-plant with the same results and with no great problems. So the F-emission of our site is reduced from approx. 50 to 1 kg/h within a year.

*) J. Ando and T. Akiyama, ISMA 1971, paper no. 1
i.d. Bull. Chem. Soc. Japan, vol. 45, 2915-2920 (1972).

Tabel 3.: Emission figures (kg/h) of effluent gasstream after application of the split-feed system (January - March 1979).

Date	F	NH ₃	SiO ₂	Cl	off-gas m ³ /h	Product
17-1-'79	0,07	0,25	0,04	0,11	90.000	12+10+18
22-2-'79	0,29	0,23	0,17	0,08	94.000	15+15+15
1-3-'79	0,34	0,17	0,28	0,10	90.000	15+12+24
12-3-'79	0,17	0	0,26	0,21	80.000	15+12+24

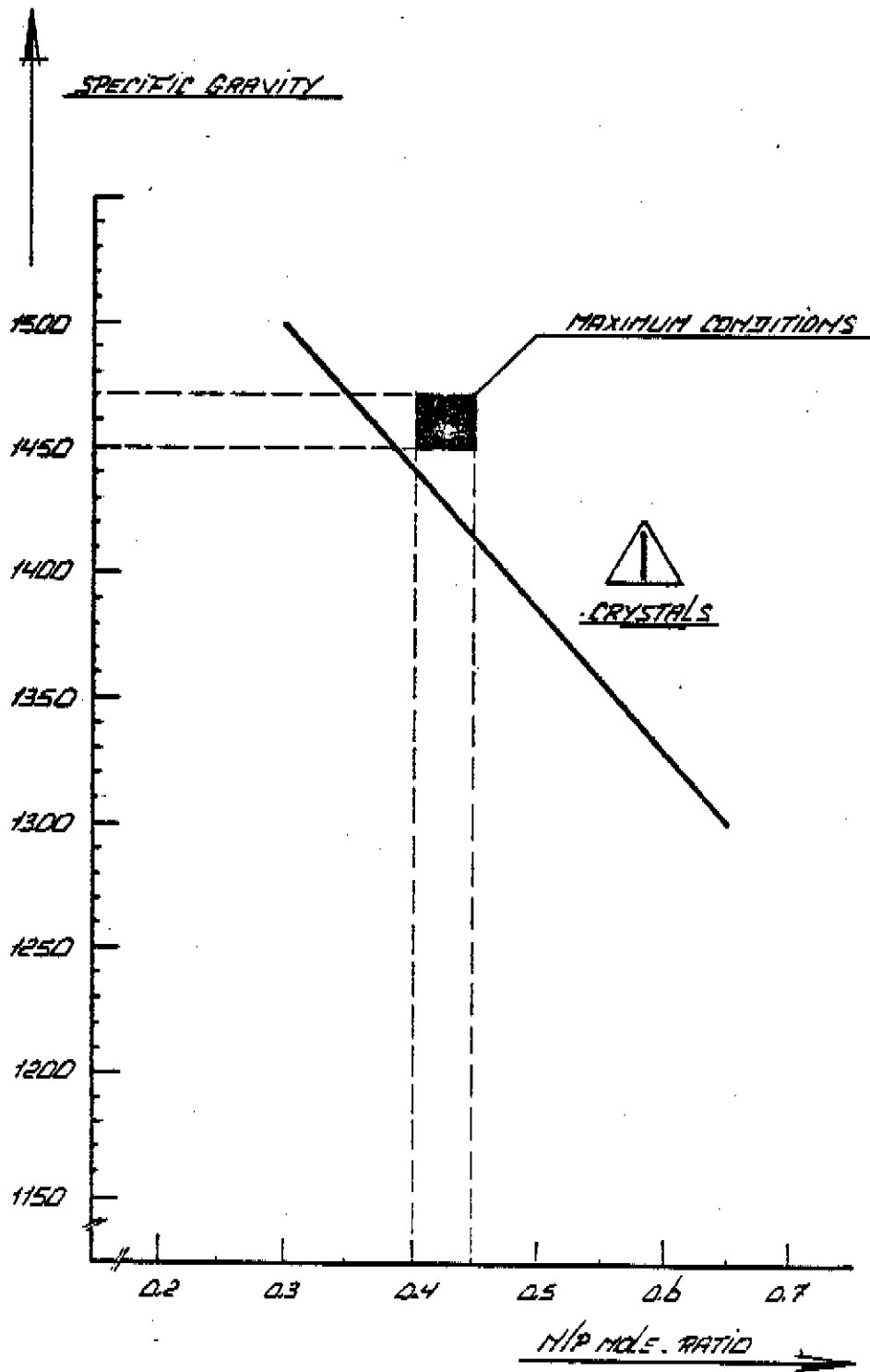


Fig.3. Operation conditions scrubber liquid for the split feed system.

USE OF WEAK ACID

When we use weak acid for the absorption of NH_3 we are confronted with blockages in the impingement plate scrubber. In our laboratory experiments using weak acid (33% m/m P_2O_5) we also found a crystalline compound. X-ray analysis revealed it to be an until now unknown compound with the approximate composition $8(\text{NH}_4)_2\text{SiF}_6 \cdot \text{K}_2\text{SiF}_6$, mixed crystals. Soon after the start of the plant trials with weak acid the impingement plates in the scrubber blocked with salt of the same composition 8.1. To overcome these troubles we first tried to remove the H_2SiF_6 from the weak acid by precipitation with Na_2SO_4 but this would be a too complex operation. Fortunately however we also run a diammonium phosphate plant which also has been changed to the split-feed system in order to meet environmental regulations. In this plant the off-gases are not scrubbed in a impingement plate tower but with spray-nozzles in the gas channels. Here also the 8.1 salt was found in the scrubbing liquid however without causing blocking problems. So if in a scrubber instead of impingement plates we use properly designed spray-nozzles then a satisfactory operation with acceptable low F-emission and high efficiency absorption of NH_3 can be attained. This can also at the same time be achieved with weak acid, thus giving corresponding savings in concentration costs.

DISCUSSION OF THE RESULTS

Both the laboratory experiments and the plant results make it clear that phosphoric acid, neutralized to a N/P mole ratio of 0.4 - 0.6 is an excellent absorption fluid for NH_3 from off-gas streams from an NPK-granulation- of diammonium phosphate plant. Partial neutralisation decreases the HF and SiF_4 -vapour pressure of the wet-process-phosphoric acid to such an extent that the remaining F-emission stays far below the legal limits.

The use of weak phosphoric acid though containing 1.5 - 1% m/m H_2SiF_6 , further decreases the F-emission and what is more results in an appreciable saving of evaporation costs in concentrating the weak acid.

When using weak acid there appears in the partially neutralised liquid a precipitate of an until now unknown substance, a mixed crystal of composition approx. $8(\text{NH}_4)_2\text{SiF}_6 \cdot \text{K}_2\text{SiF}_6$ (8.1 salt). The K in this salt must come from the small K content of the phosphate rock or from the NPK-dust in the scrubbed gas streams. This 8.1 salt shows a remarkable low solubility as compared with pure $(\text{NH}_4)_2\text{SiF}_6$. Preliminary crystal parameters suggest a hexagonal structure, being isomorphic with the low temperature modifications of both $(\text{NH}_4)_2\text{SiF}_6$ and K_2SiF_6 . About this new compound we hope to publish a separate paper shortly. In practice it has been shown that the nuisance of these precipitate formations can be avoided by the use of spray-nozzles instead of impingement plates in the scrubber and gas channels.

The procedure as explained above resembles in some aspects those described in a Japanese Patent (JA51/65.009; 1974 Mitsui Toatsu Chem Inc.) and a British Patent (GB 1.019.318, ICI, 1963). In the Japanese Patent the scrubbing liquid is prepared separately by neutralising part of the phosphoric acid with ammonia till N/P mole ratio 0.3 - 0.8. Here it was also found that by adjusting the mole ratio mist or fog formation can be avoided. The nature of the mist or fog was not clarified. In the ICI-patent the limits for the $\text{NH}_4/\text{P}_2\text{O}_5$ -mole ratio are stated 0.25 - 0.5 at 50°C corresponding with a N/P mole ratio of 0.125 - 0.25. The upper limit is dictated by the observation that above this limit crystal precipitation of NH_4 -phosphates occurs which could cause fouling and choking of the scrubber. In our experience this N/P mole ratio is too low for optimal performance. Also it is clear from the solubility diagrams of NH_4 -phosphates that at the equilibrium temperature the solution is still far from saturation, so that crystallisation of monoammonium phosphate is not to be feared. One has only to beware of the drop in temperature during plant stops at N/P mole ratios higher than 0.8 - 0.9. We suppose that the crystal precipitations mentioned above in the ICI-patent could have been our 8.1 salt instead of ammonium phosphate. In the two patents there is no indication that the mist is formed of $(\text{NH}_4)_2\text{SiF}_6$ as we found. Only NH_4Cl is suspected.

The most simple practical application is to feed the acid into the mixing tank, avoiding every contact between the NH_3 -containing air stream and fresh acid. From the mixing tank the liquid with the right N/P mole ratio is fed to the scrubber. The feed-rate is adjusted in such a way that a constant N/P mole ratio in the circulating liquid is maintained. The procedure make scrubbing with other acids like H_2SO_4 , as mentioned in literature*) superfluous. This is a great advantage to the ultimate quality of the fertilisers made in this process. A high proportion of sulphate in combination with ammoniumnitrate must be avoided because of enhanced plasticity during some period after production.

*) Chem. Eng., 85, 31 (1978).

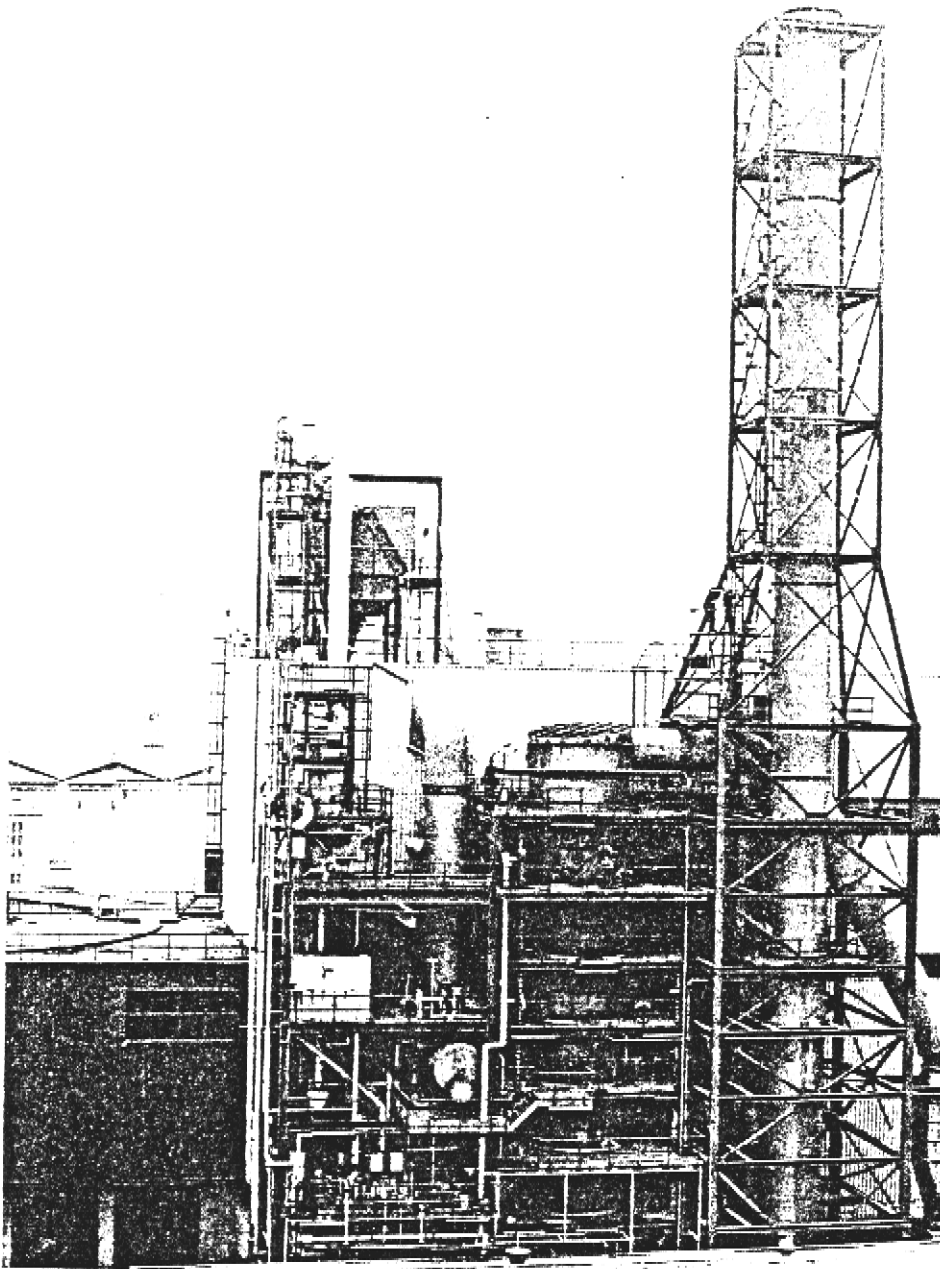


Fig.4. View on the new UKF-NPK-plant with on the foreground the effluent gas scrubber and the stack.

TA/80/15 Fluorine emission control of the new UKF-NPK plant at Pernis, Netherlands by J.Th. BOONTJE, Th.J. THOONEN, UKF, Netherlands
DISCUSSION : (Rapporteur R. Schoemaker, UKF, Netherlands)

Q - Mr. J.W. BAYNHAM, Scottish Agricultural Industries, United Kingdom

In you paper you do not indicate whether you have examined the effect on F-emission of using phosphoric acid made from different phosphate rocks?

Does the higher N/P mole ratio continue to have the same beneficial effect on reducing F-emission even when the fluorine is present primarily as F rather than as silicofluoride?

A - We did our experiments only with the acid actually produced from Khouribga/Zin phosphate. This acid contains a surplus of F over H_2SiF_6 .

It is especially the H_2SiF_6 which contributes to the high volatility of F from phosphoric acid. Remember the fact that the mist consists almost completely of $(NH_4)_2SiF_6$. We do not fear much trouble from the less volatile HF, which is also bound more firmly with iron and aluminium (see also paper 11). From table 2, on page 15-9, you can see from the composition of the scrubbing liquid that in the first eight experiments, there is always an overstoichiometric amount of F present above the composition H_2SiF_6 (10% ratio F : $SiO_2 = 1.9$) but F is only released from the liquid in the mole ratio of H_2SiF_6 with SiO_2 .

Q - Mr. K. CONSTANT, Fedmis, South Africa

Pipe reactor: there is a trend towards pipe cross reactors, making use of both phosphoric acid and sulphuric acid. It is claimed that the sulphate is required to improve the pipe reactor performance, especially in view of scaling problems. Have you tried the addition of H_2SO_4 ? Do you add liquid or gaseous NH_3 to the pipe reactor?

Plasticity caused by sulphates: we found that the presence of sulphate especially $(NH_4)_2SO_4$ reduces plasticity and helps to avoid overgranulation. By adding $(NH_4)_2SO_4$ to our formulations we can increase production rates by up to 15%. What is your comment?

A - We did not use up till now the pipe cross reactor in the plant. We did not have scaling problems, probably because our acid is low in Fe and Al. In the plant, we are using liquid ammonia for the pipe reactor. In pilot plant scale, we made very successful trials with gaseous ammonia and also with the pipe cross reactor in making high sulphur compositions.

This different experience with sulphate can stem from a different plant design. We have indeed evidence that in a granulation with high ammonium nitrate containing fertilisers, with a high proportion of fluid phase in the granulation step ammonium sulphate can be of value reducing overgranulation. But we did not find in general a beneficial effect on plasticity. Residence time at a high temperature can probably be an answer to overcome plasticity problems by approaching the more stable composition.

Q - Mr. R. SACELDO GOMEZ, ERT, Spain

On page 3, you mentioned two pipe reactors per MAP-spray. What is the reason to use 2 reactors instead of one?

A - There are two pipe reactors installed for the reason that we need a larger turndown ratio than the 50% you can achieve with one pipe reactor, because the plant makes a wide range of different products.

Q - At page 4, you mention different concentrations of acid from 35 to 50% P_2O_5 as feed to the T-reactor. Can you say what is the optimal moisture in the bed granulator for the different formulations?

A - This question is not easy to be answered, because it is different for every grade we make. Moisture content is about 1.5% in the granulator but the deciding factor is the wt% fluid phase depending on the solubility of the granulation mix.

Q - Mr. O. NEVES, Luchsinger, Brazil

Can you develop two points:

- Type of scrubber used;
- Relation between phosphoric acid and gas flow in scrubbing?

A - Originally a Peabody scrubber was installed. After the troubles with the 8.1 salt blocking the impingement plates, these plates were removed from the lower section, where the acid scrubbing was performed. The upper section has still the impingement plates. The last traces of F are washed from the air with river water, which with its very low F-content flows back into the river. The gasflow is about 120,000 m^3/h ; this is scrubbed with about 200 m^3/h circulating liquid. The addition of make-up acid is about 2 m^3 30% P_2O_5 depending on the NH_3 -content in the gasstream.

Q - Mr. P. MORAILLON, Générale des Engrais, France

Are the two impingement plates used to stop the fluorine at the upper section of the gas scrubber well fed with waste water? What happens with the resulting polluted water?

Would it not be preferable to modify the composition of the washing liquid at the lower section to reduce the fluorine emission almost to nil and to use the upper section to stop the P_2O_5 and the residual ammonia entrainment with an appropriate washing liquid which would be recycled at the lower section?

As an information, a russian paper published in 1971 establishes the correlation between fluorine emission and the atomic N/P ratio in the washing liquid (Summary N° 931, Fertilizer Abstracts, June 1973).

A - The two impingement plates in the upper section of the scrubber are maintained. In this section the remaining evolved F is absorbed with an efficiency better than 95% with river water. This water with acceptable low F-content flows back into the river. Recycling this water to the plant is at this moment not practicable due to higher evaporation costs.

Q - Mr. S. ARNON, Fertilizers & Chemicals, Israel

Is it necessary to cool the granulate in all kinds of NPK produced?

A - No, only in the cases where there is too high a fluid phase content in the granulate, due to a high soluble salt content, viz. ammonium-nitrate rich compositions. In these cases, we cool in order to prevent fouling of the sieves and to lower the temperature of the recycle.

Q - In you paper, you state that the TVA pipe reactor is not practicable in making DAP - Can you explain?

A - With the TVA-pipe reactor, it is of course possible to make diammonium-phosphate in a two stage process, but the solution we choose was better for our situation to get high mole ratio; working with the horizontal TVA pipe reactor we did not get always a stable operation. We build in a static mixer in the outlet of the pipe reactor to improve mixing and reaction and to give some back pressure. With this configuration, we achieved satisfactory results.

Q - Mr. J. OLIVARES, E.R.T., Spain

We are employing in our plant 35-50% wet phosphoric acid to feed the "T" reactor with about 5% of solids. What is the acid composition in terms of solid content in your case?

A - The actual solids in the feed to the pipe reactor is measured to be about 3 wt%.

Q - Mr. A. BARBERA, Montedison SpA, Italy

The paper describes a new salt with the following composition $8(\text{NH}_4)_2\text{SiF}_6 \cdot \text{K}_2\text{SiF}_6$. Are you sure the salt is really new or might it be simply a solid solution? Can you give or send us diffraction data?

A - All evidence points in the direction of a solid solution or mixed crystal, that is the same. We could establish a range of at least 1 : 1 to 8 : 1 mole $(\text{NH}_4)_2\text{SiF}_6$ to mole K_2SiF_6 with a corresponding range of coexisting solutions. The mixed crystal phase is clearly isomorphous with the low temperature -modifications of both $(\text{NH}_4)_2\text{SiF}_6$ and K_2SiF_6 , existing in pure form, respectively below a temperature of 13° and 10° C. The -phase with both NH_4^+ and K^+ -ion seems to be much more stable, even at temperature exceeding by far the above mentioned transition points. Remember that we found the 8.1 salt at a temperature of 50° C in the scrubber liquid. For pure scientific reasons, it would be interesting to investigate the whole temperature range and also in solutions containing partially ammoniated phosphoric acid for practical reasons. Theoretically, it might be expected that above a certain temperature there must exist a continuous area of $-(\text{NH}_4)_2\text{SiF}_6$ and $-\text{K}_2\text{SiF}_6$. Perhaps it only exists under pressure because otherwise pyrolyse of the silicofluorides would happen. The mixed crystals can very easy be prepared f.e. by adding solid K_2SiF_6 to a 2-18 w.% solution of $(\text{NH}_4)_2\text{SiF}_6$ in water at ambient temperature. Under the microscope in polarized light after a few minutes, you can see the growing of the hexagonal double refractive mixed crystals.

Q - Mr. C. DEBAYEUX, CdF Chimie, France

p15-14 you state that "a high proportion of sulphate in combination with ammonium nitrate must be avoided...". Can you indicate (in %) the limit of the ratio SO_4 mole : NO_3 mole?

A - We do not have figures about this ratio.

Q - Mr. L. THIRAN, Société Carbochimique, Belgium

I would like to receive some characteristic figures of the compounds NH_4 , K-fluosilicate.

A - The X-ray diffraction figures were distributed at the conference.

Q - Mr. B. AVENBERG, Supra, Sweden

Could you explain the benefits of having two nozzles in your pipe reactor?

A - We are using a pipe reactor with two outlets in order to get a better distribution of the ammoniated slurry over the beds. When we direct the stream on one spot the bed is disturbed by the vigorous outflow of the pipe reactor.

Q - Mr. F.G. MEMERILLERA, S.A. Cros, Spain

You say in your paper that the use of diluted phosphoric acid saves energy. Do you not need to remove the excess of water at the dryer with lower efficiency, than in the phosphoric acid concentration or to use a higher ammonium nitrate concentration for the same grade and formulation?

A - The heat balance is just in equilibrium by using an average of about 44% P_2O_5 , that is to say that the heat of neutralisation is sufficient to evaporate the water in the resulting ammonium phosphate slurry to dry. When we used concentrated acid, we used water for dilution and scrubbing. Now we use weak acid instead of water. If we can concentrate this to about 38% P_2O_5 , we can on the average mix up 1 part of this acid with 1 part of concentrated acid of about 54% P_2O_5 .

Q - Is there any explanation for the ammonia losses, the result of your laboratory test, table 2, being higher at lower N/P mole ratio in case of concentrated phosphoric acid?

A - At the lower N/P mole ratio, the NH_3 is trapped by H_2SiF_6 vapour forming a mist of crystalline $(\text{NH}_4)_2\text{SiF}_6$, not to be absorbed in the scrubbing liquid. So F, SiO_2 and NH_3 escape simultaneously and are in one compound found in the Soxhlet filter. The condensate is mainly H_2SiF_6 .

Q - Why is in the dilute phosphoric acid experiment the NH_3 -% in the condensate the opposite?

A - When there is no mist formation left then it is a matter of real NH_3 -absorption efficiency in the scrubbing acid. The condensate contains more NH_3 than according to $(\text{NH}_4)_2\text{SiF}_6$ so there is free ammonia left.

Q - Mr. G. BRUSASCO, Montedison SpA, Italy

The use of one tower for all the gaseous effluents coming out of the plant is very interesting.

1. What is the flowrate of pre-ammoniated phosphoric acid through the tower?
2. What is the maximum allowed temperature on the gases coming from the dryer and the tower construction materials?

A - The flowrate is about 200 m³/h for about 120,000 m³ offgases. The temperature of these offgases from the dryer is about 70-90° C. The tower is made of rubber lined steel.

Q - Mr. A. BARBERA, Montedison SpA, Italy

The paper shows how, at your new NPK plant, NH₃ fumes are recovered absorbing them with H₃PO₄ at a given N/P mole ratio in the range 0.4-0.6.

Do you determine N/P ratio with an automatic system of analysis? If you do so, can you tell us if the automatic analytical results are used "on line" for an automatic control (regulation) of the N/P ratio.

A - The N/P ratio is not analyzed automatically. Once our samples were taken and automatically titrated by the plantshift operators. The accuracy is sufficient because of the large hold up of circulating liquid in the scrubber system, including the mixing tank.

X-ray pattern of hexagonal compounds of the type M_2XF_6

Indices hkl (large C)	$\beta\text{-K}_2\text{SiF}_6$	$\beta(\text{NH}_4)_2\text{SiF}_6$ K_2SiF_6	$\beta\text{-(NH}_4)_2\text{SiF}_6$	$(\text{NH}_4)_2\text{GeF}_6$	K_2GeF_6	Indices hkl (small C)
	A = 5.67 C = 9.27 1/2 C = 4.63	A = 5.82 C = 9.46 1/2 C = 4.73	A = 5.77 C = 4.79	A = 5.862 C = 4.817	A = 5.632 C = 4.668	
100	4.94	5.04	5.00	5.07	4.89	100
002	4.65	4.73	4.79	4.81	4.667	001
101	4.33	4.45	-	-	-	-
102	3.36	3.45	3.45	3.49	3.371	101
110	2.84	2.91	2.88	2.932	2.815	110
103	2.61	2.67	-	-	-	-
200	2.44	2.52	2.498	-	-	200
112	-	2.477	-	2.503	2.410	111
201	2.37	2.436	-	-	-	-
004	2.32	2.366	2.394	2.407	2.333	002
202	2.165	2.225	2.215	2.246	2.161	201
104	2.099	2.142	2.159	2.176	2.105	102
203	1.924	1.968	-	-	-	-
210	1.859	-	-	1.919	1.844	210
114	1.789	1.836	1.842	1.862	1.797	112
212	1.726	1.768	1.757	1.783	1.715	211
204	1.687	1.726	1.729	1.748	1.686	202
300	1.642	-	-	1.692	1.6260	300
301	-	1.653	-	-	-	-
213	1.591	1.630	-	-	-	-
006	-	-	1.596	1.605	1.5558	003
205	1.479	1.513	-	-	-	-
302	-	-	1.573	1.597	1.5352	301

Lattice constants in Å