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THE PRODUCTION OF ALUMINIUM FLUORIDE FROM  
WASTE GASES OF PHOSPHORIC ACID PLANTS

by R. RICHTER (Vöest-Alpine - Austria)

The waste gases containing fluorine are an important factor of the modern phosphate industry.

Depending on their origin, rock phosphates contain 2.5 - 4.4 % fluorine in the form of fluorapatite.

Considering that in the year, 80 million tons of rock phosphate have been hauled, this represents a total of approximately 2.5 million tons of fluorine.

For comparison, in 1973, only 1.6 million tons of fluorine were hauled in the form of fluorite, containing approximately 47 % fluorine.

Therefore, rock phosphate is not only the raw material required for the phosphate industry, but could also represent an essential raw material source for the fluorine chemistry.

During the hydrolization of rock phosphate to phosphoric acid and further treatment to superphosphate/triple superphosphate, a more or less great portion of fluorine contained in rock phosphate is collected in the waste gases in the form of silicon tetrafluoride ( $\text{SiF}_4$ ) as by-product.

The remainder of fluorine is present in the final product.

Figure 1 shows the distribution of fluorine over the different kinds of products of various processes. Here, we note that waste gases only contain relatively small amounts of fluorine; approximately 25 % during the production of superphosphate and 13 % during the production of triple superphosphate. A large proportion, approximately 40 %, accrues during the production of phosphoric acid, especially if the phosphoric acid is concentrated up to 55 - 57 %, as it is usual.

The proportion is also quite considerable during the production of triple superphosphate, up to 60 %, when superphosphoric acid is used as raw material. The fluorine content in the waste gases is increased by adding silicic acid during the hydrolization of rock phosphate. Due to technical reasons of process, the addition of silicic acid is often very advantageous.

Thorough tests have shown that, during the production of superphosphate, an increase from 25 to 40 % and, during the production of phosphoric acid, an increase from 40 to 70 % may be expected.

In all cases however, the major portion of silicon tetrafluoride ( $\text{SiF}_4$ ) accumulates in the waste gases of the phosphoric acid plants and especially in the waste gases of the concentration stage of phosphoric acid.

Silicon tetrafluoride ( $\text{SiF}_4$ ) is a very toxic compound and should definitely be removed from the waste gases, particularly in view of the environmental pol-

lution problems. For this type of waste gas cleaning, there is also an essential economical incentive, since it is possible to recover part of the fluorine from the rock phosphates. Here, rock phosphate may partially be used as fluorine raw material. Eventually, a reduction of the phosphoric acid price and/or of phosphate fertilizers will be possible, when both products  $P_2O_5$  and F are a combined factor of calculation.

The purification of waste gases from phosphate plants is one of the very rare cases when the solution of an environmental problem may at the same time bring about an improvement of the economy of the process and, above all, a new source of raw materials.

The technical recovery of silicon tetrafluoride from waste gases is relatively simple, as gas scrubbers are used. Various types of problem, according to different processes, are involved. It is of great importance that silicon tetrafluoride ( $SiF_4$ ) contained in the waste gases generates hexa-fluoro-silicic acid ( $H_2SiF_6$ ) and silicic acid ( $SiO_2$ ) during the absorption with water. The silicic acid produced tends to incrustate and clog the scrubbers. Therefore, generally Venturi-scrubbers are used. The recovery of fluorine from the phosphoric acid concentration is slightly more difficult, since the evaporation is carried out under vacuum and the waste gases contain phosphoric acid mists. Here, wash towers are used, into which wash liquor is injected through several nozzles.

In any case, a solution of approximately 25 % of hexa-fluoro-silicic acid is obtained for further treatment. However, this solution has the great disadvantage of being very corrosive. Furthermore, the fluorine content is very low, so that long distance transportation is not advisable. Therefore, this solution must be treated in situ. The plants for further processing must be technically simple and should operate at low maintenance costs, so that an economical operation is possible for smaller capacities as well.

Direct use of aqueous acid solution is not possible, except for small ranges of application, such as for building preservation and drinking water fluoridation.

The following possibilities of use for hexa-fluoro-silicic acid are well known:

The production of calcium fluoride from hexa-fluoro-silicic acid was worked out especially by the US-Bureau of Mines. About 15 years ago, a process was developed which could not be implemented so far, since the costs of the synthetic calcium fluoride are higher than the market-price of the natural product.

Processes for the production of hydrogen fluoride from hexa-fluoro-silicic acid have been developed in theoretically. The processes themselves are very interesting, but, they show deficiencies which jeopardize their economy. None of these processes have been implemented so far. New developments on this field may be expected in the future.

The production of aluminium fluoride or cryolite presently represents the only tested processes for utilizing hexa-fluoro-silicic acid. Aluminium fluoride and cryolite are products of great importance for the industrial production of aluminium and possess market-value therefrom. The production processes named above

are very interesting from the economical point of view as well.

A process for the production of aluminium fluoride is offered by VÖEST-ALPINE, based on the process developed by the ÖSTERREICHISCHE STICKSTOFFWERKE in Linz.

Figure 2 shows the process flowsheet of the plant :

the 25 % hexa-fluosilicic acid coming from the scrubber is pumped out (2) from the storage tank (1), pre-heated up to 65 - 75° C in the heat exchanger (3) and conveyed into the reaction tank (5) via the measuring tank (4).

Due to the reaction rate, the required reaction temperature must be at least 60° C. The reaction is exothermic, so that the temperature rises quickly up to 100° C after aluminium hydroxide has been added. After 10 - 15 minutes, the reaction has practically reached its final stage. The precipitated silicic acid which is readily filterable, is separated on the peeling centrifuge (6) and then washed with hot water.

Depending on the reaction temperature, the precipitated silicic acid show a completely different filtration behaviour. For reaction temperatures below 60° C, it is jelly-like and practically not filterable. Between 60° and 90°, it is easier to filter but does not separate quickly enough. Only when the silicic acid is heated to the boiling point of the solution (namely, up to 100 - 102° C), it adopts a solid structure, which is well filterable and may be separated without difficulty in a peeling centrifuge, just like a crystalline product.

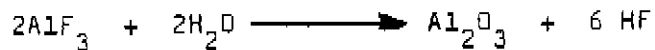
The aluminium fluoride solution and wash waters coming from the peeling centrifuge are directed to the heated crystallizers (7). One crystallizer is filled at a time and provided with seed crystals. Crystallization is achieved after 4 - 5 hours ; the solution temperature must be maintained at 90 - 95° C during this time. The separation of aluminium fluoride from its solutions is a very complicated procedure, since this is not a standard crystallization, but an internal rearrangement with subsequent crystallization of the resulting  $AlF_3 \cdot 3H_2O$ . The rate of crystallization is affected by seed crystals and by the temperature and pH-value of the solution. Higher temperatures and lower pH-values act accelerating.

The aluminium-fluotrihydrate shows a grain size of 50 - 90 microns; it is separated on the peeling centrifuge (8) and conveyed into an intermediate tank (9). Mother liquor from the crystallization stage may partially be recycled into the scrubber, for the production of fluosilicic acid, whereby fluorine and aluminium still present are recovered. Part of the mother liquor must be abandoned to keep the pollution level constant.

First of all, the adhesive humidity is removed from the aluminium-fluotrihydrate in the drier (10) at approximately 100° C, then, the crystallization water is expelled in a two-stage fluidized bed furnace (11). The fluidized bed furnace is heated up with combustion gases, heated in the air pre-heater (12) and in the heating muffle (13).

The major quantity of water is separated in the primary fluidized bed furnace between 135 - 205° C. The residual water is very strongly combined and the product is heated up to 570 - 600° C in the secondary fluidized bed furnace, in order to achieve a desired residual water content of less than 0.5 % by

weight. There is a great danger of hydrolytical fluorine splitting at these high temperatures and large surface of fine-grain aluminium fluoride :



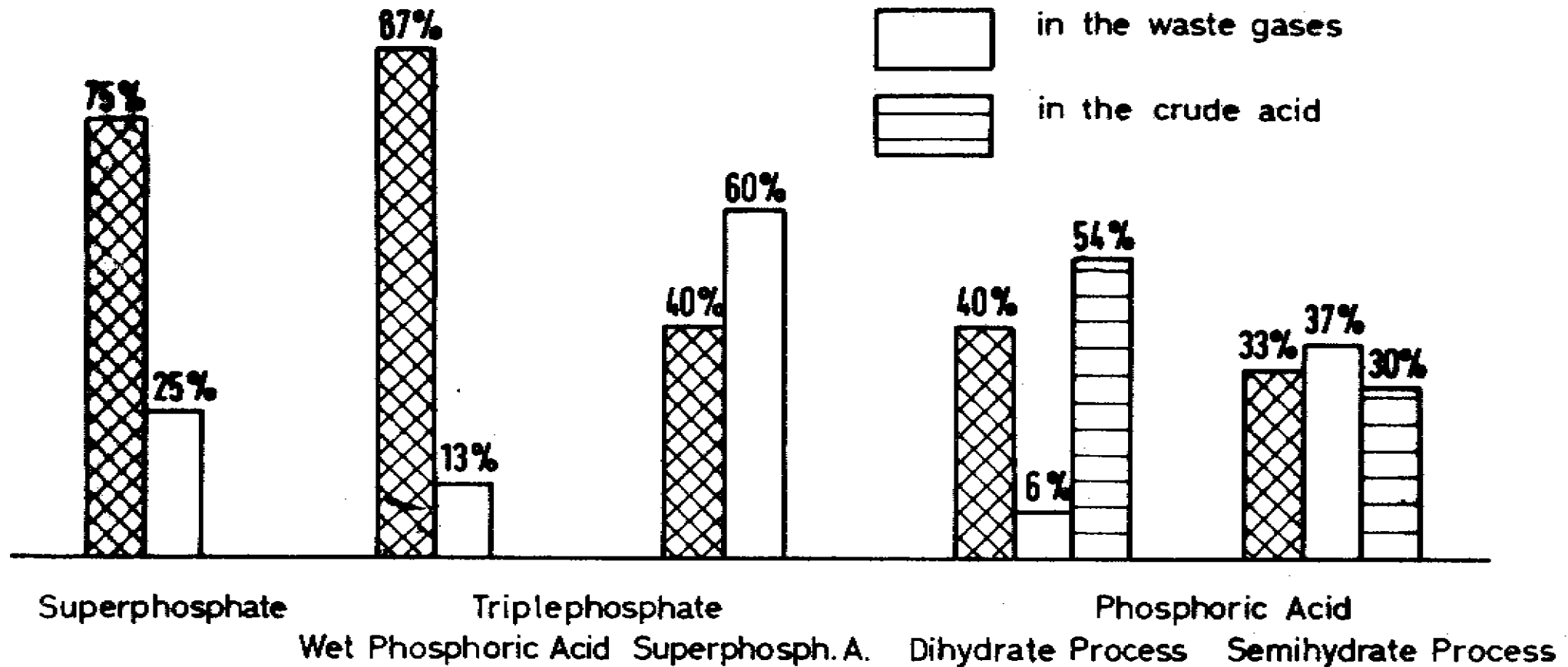
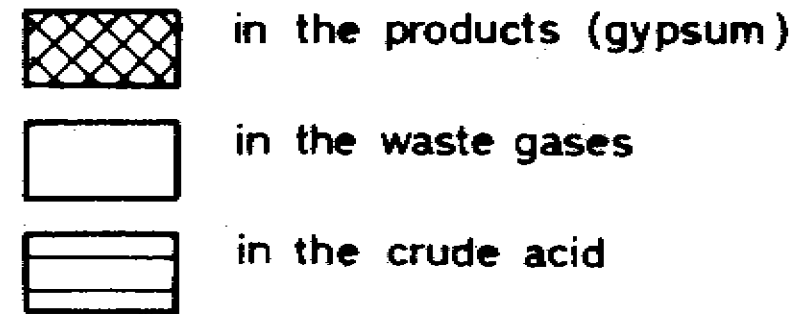
The fluorine loss may be kept low, however, when the calcination vapours are quickly removed through the supporting gas of the fluidized bed. Since the trihydrate contains approximately 40 % by weight, the heat consumption of calcination is very high : approximately 1,000 kcal are fed for each kg of finished product.

The flue gas of the fluidized bed furnaces is cooled in an injection cooler and blown over the roof. Likewise, all dust particles, waste gases, steams and vapours are collected in a common waste gas line and neutralized in a wash tower filled with limestone. To simplify these matters, apparatus and the pertaining lines are not shown in the flowsheet. The finished product is cooled in the cooler (14) and bagged.

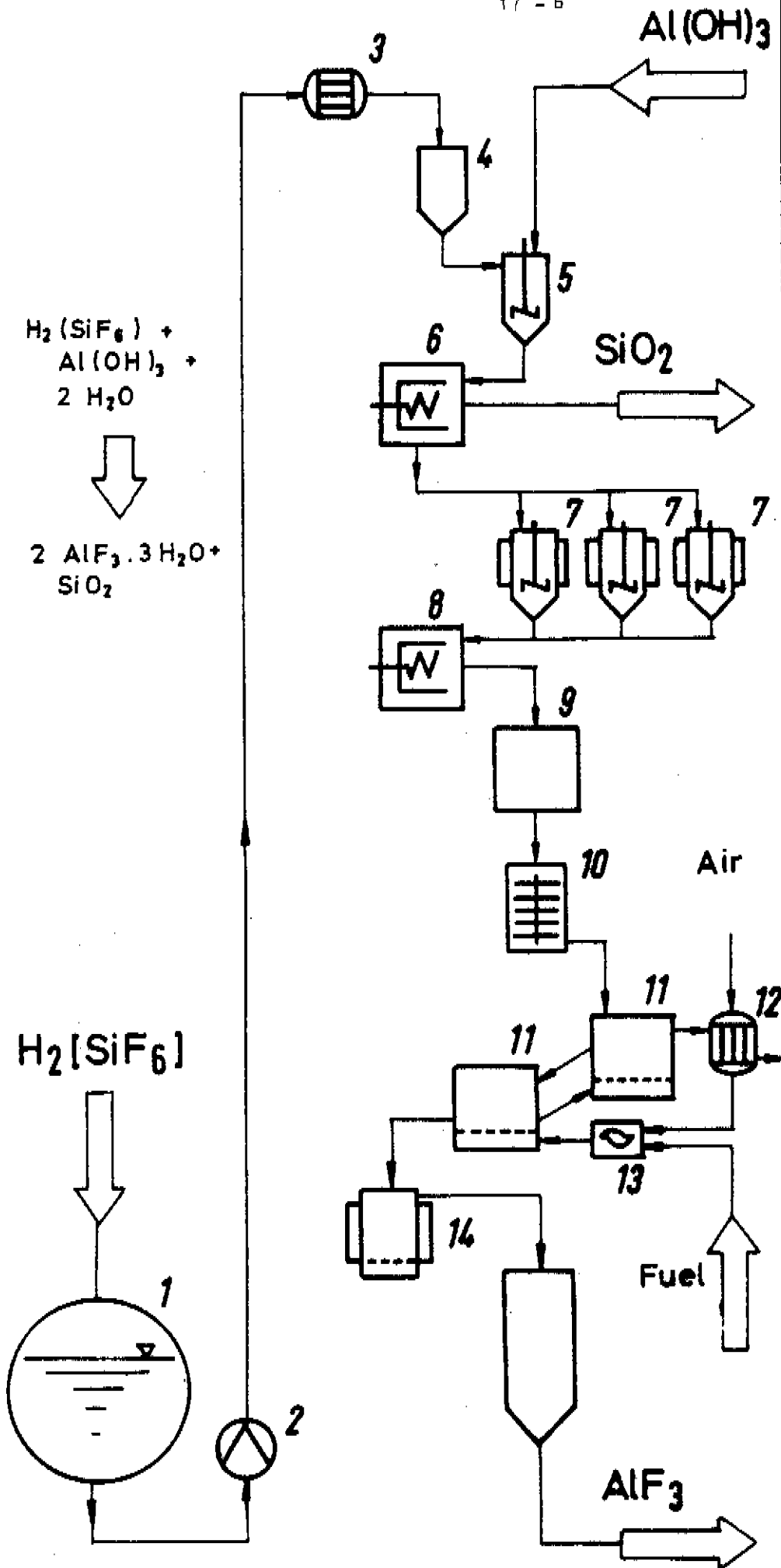
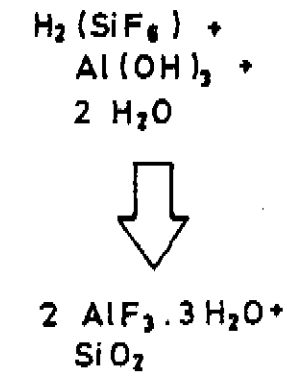
The characteristic data of the finished product and the consumption figures for the auxiliary and operating materials are shown in table 3.

The process described has been in operation for 10 years at the ÖSTERREICHISCHE STICKSTOFFWERKE in Linz to the full satisfaction of everyone. Several plants, all of which operate according to the same process have already been put into operation in different countries.

There are no corrosion problems in the plant. The equipment in the liquid part consists of rubberlined steel, the heat exchangers (3) of graphite, the calciner of special steel and the cooler (4) and bagging bin are of aluminium.



Flow-Sheet  
of a  
VÖEST - ÖSW  
AlF<sub>3</sub> - Plant



Consumption Figures for 1,000 t  $AlF_3$

$H_2[SiF_6]$ , 100 %	t	1,10
$Al(OH)_3$ , 100 %	t	1,17
Steam, 3 atm	t	1,5
Electric Power	kWh	212
Water	$m^3$	100
Fuel Gas	Gcal	1,5

Typical Analysis of the Final Product

$AlF_3$	%	97...98
$SiO_2$	%	< 0,1
$Fe_2O_3$	%	< 0,01
$Al_2(SO_4)_3$	%	< 0,05
Humidity	%	< 0,5
Particle-Size Distribution	$\mu m$	40...100

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Discussion.

Dr. Richter (Voest Alpine, Austria)

Phosphate rocks presently used contain from 2 to 5% F in the form of fluoapatite. When phosphate is reacted to produce phosphoric acid, single and triple superphosphate, part of the fluorine evolves as  $\text{SiF}_4$  in the exhaust gases of the plant. This part can be recovered. The remainder goes into the finished product and is lost as a fluorine raw material.

Slide f shows the distribution of fluorine according to the stages of production in the various products. In the case of single superphosphate 25% F is evolved in the gases, 13% in the case of triple superphosphate. In the manufacture of superphosphoric acid this figure is increased to 60%. In phosphoric acid plants it amounts to 6% before concentration and averages 37% after acid concentration. This morning we heard that in the new Fisons process, it can increase to 70%, which can be very important when F is recovered. Assuming that, as an average for all processes, it is possible to recover 30%, this means a total annual tonnage of recoverable F of about one million t. Considering that 1.4 million tons is produced annually from fluorspar, rock phosphate can be a substantial source of fluorine. Unfortunately at present this fluorine source can only be partly used for lack of a convenient  $\text{SiF}_4$  treatment process. The process for producing aluminium fluoride is the only one which can be regarded as technically sound. It was developed a few years ago at Chemie Linz and is operated in several plants all over the world. Voest Alpine builds these plants as Chemie Linz licences.

The first stage of the process is the technical recovery of  $\text{SiF}_4$  with scrubbers ; there are now scrubbers, such as the Swift scrubber, which do a good job. The rate of recovery is about 90 -95% according to the concentration of hexafluosilicic acid, which must be around 20% in view of the overall plant efficiency.

The solution itself is very unpleasant, because it is corrosive. Since the F content is rather low, long distance transport is not economical and the treatment must be done on production sites. The plants must be simple since they are a modest additional facility for phosphoric acid producers and the plants should operate at low cost. These requirements are completely met in the process described here. The plant operates batchwise and is reloaded every 30 min. Fluosilicic acid contained in a surge tank is pumped into the reaction tank after passing through a heat exchanger and a measuring tank.  $\text{Al}(\text{OH})_3$  is fed in the reaction tank. The reaction is exothermic. The temperature increases rapidly to 100° C, and that temperature must be maintained as closely as possible to promote the formation of filterable  $\text{SiO}_2$ . Hard crystals are then formed which can be separated in the centrifuge. The solution is then fed in three or four crystallizers where after crystal seeding, aluminium fluoride is produced in the trihydrate form. This stage of the process must also be operated very carefully from the temperature viewpoint, 90 - 95°C, so the rate of reaction is satisfactory. The reaction lasts five to six hours and the product may be distributed in as many as four crystallisers.

All chemists know that  $AlF_3$  separation is a very difficult process. I already stated that the reaction takes place only with seed crystals. When the reaction is achieved completely the suspension is fed into a peeling centrifuge where it is separated from the mother-liquor. The trihydrate has a 5.8% moisture, which is removed, after passing through a surge-tank, in a pan dryer. The following pieces of equipment are furnaces to remove crystallization water. In view of the high stability of crystallization water calcination takes place in a two-stage furnace, the first at  $200^\circ C$ , the second at  $600^\circ C$ . It must be pointed out that, in the second stage, the high temperatures may result in the dissociation of F by hydrolysis, which is avoided by expelling quickly the water with the supporting gas of the fluidized bed.

Calcination uses a lot of energy, about 1000 Kcal/kg product. Anyway 40% by weight of crystallization water must be separated.

Slide 3 shows the raw material consumption and the quality of the product obtained. I would like to say that in the last plants built, the efficiency was improved in so far as the mother liquor of the second centrifuge follows a circuit via the scrubber. Thus 50 - 80% of the mother liquor is left in circulation so that the amount of impurities is reduced, in particular chlorides and, possibly, sulphides. The remainder of the mother liquor, 20 to 50%, must be disposed of. Without neutralization, it cannot be thrown away with waste waters. The consumption figures quoted in the pages 1.1. and 1.17, can be improved to 0.98 for fluosilicic acid and 1 for  $Al(OH)_3$  expressed in tons of raw material per ton of finished product.

Finally, regarding raw materials, I should stress that these substances are very corrosive but the initial corrosion difficulties can be considered as sorted out. They related to mild steel equipment which should be lined with rubber. The lining should be very hard in the case of the autoclave. In the same way, pipes, pumps and centrifuge casings are made of rubber lined mild steel, pump rotors preferably in hastelloy, centrifuge rotors in 44.77 steel, a stabilized acid resistant titanium steel. With this selection of materials, maintenance problems are solved and the plant can operate for reasonable periods.

Mr. Uusitalo (Kemira Oy, Finland)

It is very well known to many of us here, that very much work has been done in Austria in the last ten years for the recovery of fluorine from waste gases, and also that the aluminium fluoride process developed by ÖSW has been implemented with success. Many other processes have been developed for the same purpose to utilize the fluorine from waste gases. Perhaps the ÖSW process has proved to be one of the most reliable. We have no doubt about the process and its importance when we have to solve the environmental problems caused by fluorine. Therefore I would like to ask some more detailed technical questions to Mr. Richter.

1. You told that you have used Swift type scrubbers for washing the gases to get fluosilicic acid. How much fluorine is there still in the waste gases, and have you experienced some other type of scrubbers? What is the phosphorus content of fluosilicic acid?

In Finland we have today an alkalisilicofluoride-production, but we have plans to go forward to some more profitable fluorine production. Do you think that  $AlF_3$  production could be one more economical possibility?

Therefore, I am asking if you can give some values for investments and production costs to produce  $AlF_3$ .

2. You have not mentioned the phosphorus content of waste liquid coming from the separation of  $AlF_3$  crystals and also you have not made clear, what you are doing with waste liquid which you cannot use in your process. Too high phosphorus content raises environmental problems.
3. As a by-product you are getting silica. What has been the importance thereof and have you used silica in some way?

Dr. Richter

Our only experience is with the Swift scrubber and I cannot say anything about the others. I would only like to state that the efficiency of the scrubber depends on the concentration of the acid produced: a 95% efficiency corresponds to 15% concentration, 90% to 25% and 85% to 33%.

Scrubbing efficiency thus strongly decreases when the concentration increases. I already indicated that the optimum concentration for operating the plant is about 25%. As a result the efficiency of the scrubber ranges from 90 to 95%.

On the problem of the phosphoric acid purity, the following can be said. The maximum acceptable  $P_2O_5$  content of the hexa-fluosilicic acid to be processed is 150 ppm. Certainly water insoluble phosphate and aluminium salts do form and end in the finished product where they are not wanted. The steel industry sets a limit of 30 ppm.

The second question also relates to the  $P_2O_5$  content. I think I have already partly answered in the first question. I would also like to recall that the mother liquors are reused in the scrubber and, hence, very little is mixed in the waste waters.

The third question relates to silica. We have to say that we make a wide use of that product. Active silica is employed in chemistry as a filler. There is also another potential use which makes this process so attractive that silica is measured when phosphate is reacted to make phosphoric acid. The advantage is that the proportion of F removed from waste gases can increase from 40% in the conventional hemihydrate process to 70% resulting in a substantial increase in the rate of fluorine recovery.

The last economic question is more difficult to answer. The investments, the cost of raw materials and of energy are variable local factors. I would however like to quote the following estimates. The economic plant capacities are within the range 5-10-15,000 t/y aluminium fluoride. The corresponding investment for a turn key plant are in Austrian Schillings 55, 75 and 95 million. The present sales value of aluminium fluoride is 10 sch/kg and the production cost for a 3,000 t/y plant is about 7 sch/kg. You then realize that, even for such low capacities, the profitability justifies the erection of such a plant.

Mr. Jemaa (SIAPE, Tunisia)

I would like to ask two questions : the first concerns the recycling of mother liquors in general. When the plant is designed for manufacturing fluosilicic acid, is it possible to recycle all the liquor ? I mean, is it possible not to use make-up water at the level of the fluosilicic acid recovery and, hence, only to use recycled mother liquors ? This applies mainly to those countries where process water is too saline.

The second question concerns the use of by-product silica. In the case of some phosphates this silica may be mixed with the phosphate to improve fluorine recovery, but some phosphates contain too much silica. Is it then possible to use that silica for instance just before phosphoric acid concentration in order to increase fluorine recovery to that level or are there also other uses of the silica produced ?

Dr. Richter

For the first question, the total substitution of the mother liquor is not possible. Part must always be recycled, between 20 and 50% according to the amounts of impurities introduced in the process. In the recycling of the mother liquor a given level of impurities should not be exceeded. As already mentioned, this refers to chlorides, sulphates and other soluble salts. Insoluble salts end unfortunately in the finished product.

The second question concerning silica obtained after phosphate reaction, the effect depends on the rate of activity of silica. The silica produced here is very active and, in consequence, very effective.

Mr. Meidell (Norsk Hydro, Norway)

When producing fluosilicic acid from the waste gases from phosphoric acid plants, there will be more or less impurities in the acid, for instance phosphorus and sulfur compounds. What happens to these impurities in your process and how do you avoid getting them in your product ?

Can you give any figures on the emission of hydrofluoric acid and aluminium fluoride particles from this process ?

Dr. Richter

I can give you figures of a complete balance on the assumption that 80% of the mother liquor is recycled. 2.5% Al is lost with SiO<sub>2</sub>, 2.8% with the mother liquor and 3.2% in the dust of the fluidized bed of the calciner. It results in a total loss of 8.5% for the whole process. For fluorine I can give you the following figures : 2.5% with SiO<sub>2</sub>, 4.2% with the mother liquor and 3.2% with the dust, total 9.9%. If the calculation is correct, we should find the figures given in the last diagramme.

Dr. H. Schuhmann (V.E.B., Chemiewerk Coswig, G.D.R.)

Dr. Richter, from Voest Alpine, states that the rate of fluorine absorption from waste gases in a superphosphate plant is 90 - 95%. We tried to improve this efficiency.

By using a new fluidized bed absorber, tested many years in commercial plants, we have obtained efficiencies of up to 98 - 99%. In this way we improved the environment position and, at the same time, increased the production of fluorine salts from the fluosilicic acid obtained. The fluosilicic acid concentration reaches 15% by a simple stage process, 25% in a two stage process. The remaining F content in the waste gases is lower than 100 mg/m<sup>3</sup> and even lower than 50 mg/m<sup>3</sup>.

For silica obtained in the AlF<sub>3</sub> process, a filtration system was found capable of fixing the level of activity by an appropriate treatment.

Mr. Schäfer (Lurgi, G.F.R.)

I would like to give additional information on this paper which might be of general interest. We are licencees of the process and, for that reason, we studied fluosilicic acid recovery very closely. The main factor is the  $P_2O_5$  content of the fluosilicic acid which implies the use of phosphate containing less than 500 ppm Cl. At 150 ppm,  $P_2O_5$  in the fluosilicic acid the mother liquor cannot be recycled. For 100 ppm, 50% can be recycled and for 50 ppm, 80 -90%. Some plants already manage to get such low  $P_2O_5$  figures. Dr. Richter knows that very well.

If I may add something, we have built F recovery plants in superphosphate works with a 99.5% efficiency. It is, however, more difficult to reduce the  $P_2O_5$  content. 200 ppm are easily reached, 50 ppm less easily.

Mr. Morsillon (Générale des Engrais S.A., France)

Dr. Richter gave us a F balance in which the F recovery exceeds 90%. But I feel that, according to the figure given for fluosilicic acid consumption, this recovery is below 70%. Is it possible to clarify this point ?

Dr. Richter

The figures I gave at the end relate to a plant which recycles 80% of the mother liquor. Those on the last slide are without recycling. This explains this discrepancy.