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FLUORIDE OF ALUMINIUM AS A BY-PRODUCT
OF SUPERPHOSPHATE MANUFACTURE

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Introduction

Fluorine is the most electro-negative of all elements and the most reactive of them. Therefore it is natural that the manufacture of fluorine compounds and their application is steadily increasing. This fact is promoted by the advanced techniques of hydrofluoric acid preparation since the thirties and the commercial manufacture of elementary fluorine since World War II, as well as by the particular features of many fluorine compounds, e.g. the extreme resistance of many compounds of fluorine chemical reactions and to elevated temperature.

Though a fluorine content is indicated in the formulas of 115 or so natural minerals, 3 minerals containing fluorine only reach practical importance for the recovery of fluorine products, namely natural cryolite (Na_3AlF_6), fluorspar (CaF_2) and fluoroapatite $\text{Ca}_4(\text{PO}_4)_3\text{CaF}$ with average contents of fluorine of 54, 48.5 and 3.5 per cent F respectively.

The deposits of natural cryolite are practically exhausted, therefore that source of fluorine is available in a limited amount only. The world production of fluorspar ranges over 2 million tons, and that of fluoroapatite in the form of phosphate rock over 40 million tons. About the half of the mined fluorspar, that of high quality, goes into the chemical industry to be transformed practically in its total to hydrofluoric acid, which is the basic chemical for all fluorine chemicals. The rest of the fluorspar is consumed in the iron and steel and ceramic industry.

Three quarters of the world's production of hydrofluoric acid are consumed by two productions only, namely the manufacture of aluminium fluoride and of chloro-fluoro-carbon compounds. The remaining quarter of the hydrofluoric acid production is sufficient to cover the need of the industries of uranium metal, cryolite, plastics or lubricants.

The heavy increase of cooling agents consumption at present, the use of fluor-containing driving agents for spray packages, and the continuously increasing demand for aluminium fluoride by the aluminium industry influenced decisively the consumption of hydrofluoric acid and the need for high quality fluorspar respectively.

The known fluorspar deposits in the world (with a content of more than 35 p.c. CaF_2) of about 70 to 80 million tons are considerable but not inexhaustible.

Of a completely different order of magnitude are the reserves of fluorine contained in the fluoroapatite in the rock phosphates. At present the phosphate ore deposits in the world, worthy of being worked (half of them are in North Africa) are estimated up to 40 thousand million tons. This corresponds to an equivalent of fluorine of about 1,400 million tons.

The recovery of fluorine products from apatites is possible, for the present, from by-product manufacture only with processes of phosphate treatment. The actually recovered quantities of fluorine products - mainly silico fluorides - correspond only to a fraction of the equivalent of fluorine contained in the rock phosphates.

The main quantity of the fluorine remains in the phosphate fertilizer, and only that fluorine is used, of course, which is freed with the tail gas purification.

Nevertheless it will be necessary to deal thoroughly with the recuperation of fluorine products from the apatite deposits, within the next decades, taking into consideration the actual tendencies of the fluorine demand.

This paper deals with a process of preparation of aluminium fluoride from aqueous solutions of hydrofluosilicic acid, obtained in the gas purification of superphosphate plants.

A) Properties and uses of aluminium fluoride

Aluminium fluoride is a white substance of the composition AlF_3 . Under normal pressure the aluminium fluoride does not melt but sublimates at approximately 1270°C .

Aluminium fluoride is produced nearly exclusively up to now by dissolving aluminiumhydroxyde in aqueous hydrofluoric acid, crystallization of a hydrate out of these solutions, and calcination of a crystallisate at temperatures of above 600°C to obtain a practically water free product.

Five defined aluminium fluoride hydrates are known. The most stable of them is the trihydrate - $\text{AlF}_3 \cdot 3 \text{H}_2\text{O}$. It exists in a soluble~~ct~~ and in a difficultly soluble~~ct~~ form.

This fact, and the possibility of formation of metastable highly saturated solutions of aluminium fluoride, is the basis of the present production method.

Aluminium fluoride is used nearly exclusively in the aluminium industry. With the manufacture of aluminium by melt electrolysis a solution of aluminiumoxyde in cryolite ($3 \text{NaF} \cdot \text{AlF}_3$) as an electrolyte is used. With the high temperatures of the electrolysis cell of about 950°C already appreciable quantities of fluorine are lost with the cell tail gas by reason of the vapour pressure of the fluoride melt. A portion of the fluorine contained in the tail gas can be recovered by an alkaline washing process in the form of sodium fluoride. The aluminium plants purchase therefore principally aluminium fluoride.

Corresponding to the high requirement for purity in the aluminium metal, demand for the aluminium fluoride too is considerable. The technical product should correspond to the following analysis:

AlF ₃	92.0 per cent minimum
SiO ₂	0.20 per cent maximum
Fe ₂ O ₃	0.05 per cent maximum
CaF ₂	0.20 per cent maximum
SO ₃	0.20 per cent maximum
NaF + Al ₂ O ₃	6.50 per cent maximum
H ₂ O	0.50 per cent maximum

B) Fluosilicic Acid and Hydrated Alumina as Raw Materials for the Manufacture of Aluminium Fluoride

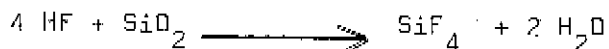
1) Fluosilicic Acid

Since more than three quarters of all phosphate fertilizers are manufactured in the form of superphosphate, the present paper refers principally to that process.

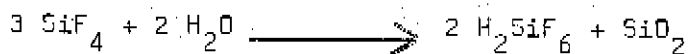
Along the general reaction:



hydrofluoric acid is formed also in the treatment of apatite of fluorine with sulphuric acid beside monocalciumphosphate and calcium sulphate. Hydrofluoric acid, according to the equation:-



is converted into the volatile siliciumtetrafluoride. This fluorine compound contained in the tail gases of superphosphate plants is removed from the tail gases by scrubbing with water. In series arrangement of such "spray" scrubbers, fluosilicic acid of approximately 15 to 23 per cent can be obtained according to the equation:-



Depending on the condition of attack and the origin of the rock phosphate a fraction only of the fluorine contained in the raw phosphate is volatilized. On an average one can count on a recovery of fluorine in the form of fluosilicic acid of about 12 per cent of the fluorine content of the raw phosphate. The rest of the fluorine remains in the superphosphate.

The fluorine obtained with the superphosphate manufacture is considered mostly as an inevitable consequence of the tail gas purification and the fluosilicic acid is processed in a

simple way to products of low commercial value, mostly to sodium silico fluoride. Up to now no economic interest existed to increase the yield of these products.

With the possibility of processing the fluosilicic acid into aluminium fluoride which is worth about four times as much as sodium silico fluoride, more favourable conditions exist and an increase in the recovery of fluorine becomes interesting.

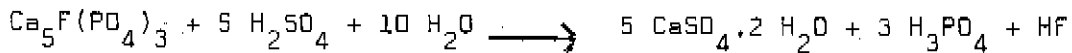
After consulting many references dealing with increases in the yield of fluorine we were able to find that e.g. a small increase in the concentration of the sulphuric acid or in the temperature of attack, and in the quantity of acid too, of course, increases the yield of fluosilicic acid. Particularly effective when processing rock phosphates poor in silicic acid, is an addition of rock phosphates rich in silicic acid or of hydratic silicic acid, as it is obtained in the manufacture of aluminium fluoride. The addition of about 1 per cent hydratic silicic acid (in relation to the rock phosphate employed) is sufficient to reach optimum yields of fluorine. Ground quartz sand, in this connection, is of no effect.

With certain rock phosphates (e.g. "SAFI" rock phosphate), and using all possibilities, we were able to increase the yield of fluorine two or three times without influencing significantly the superphosphate process.

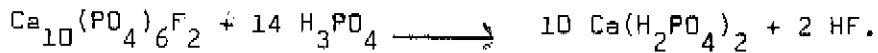
The most suitable concentration of the fluosilicic acid for the manufacture of aluminium fluoride is 17 to 18 per cent by weight. The content of P_2O_5 of the acid must never exceed 200 to 300 mg. per litre. Therefore it is necessary either to ensure that too much phosphate dust does not enter the gas washers of the superphosphate plant, or to remove the dust of the tail gas in a cyclone before it enters the scrubbers. There are no other requirements for the quality of the acid.

Though here the use of by-product fluosilicic acid from the manufacture of superphosphate, has been discussed, fluosilicic acid derived from other phosphate

processes can be used for the production of aluminium fluoride. I mentioned only the attack of rock phosphate by sulphuric acid to give phosphoric acid:-



and by phosphoric acid to give triple superphosphate:-



Here too it is possible to obtain fluosilicic acid from hydrofluoric acid via silicium tetrafluoride.

Fluosilicic acid from plants of phosphate processing contains always approximately 17 per cent more silicic acid in a stable solution as it would correspond to the formula H_2SiF_6 , stoichiometrically. Using SAFI rock phosphate for instance for superphosphate manufacture, the fluosilicic acid contains among other substances also about 0.006 grs. iodine per litre of acid, and this in the form of hydriodic acid. With a subsequent reaction with hydrate of alumina this iodine is liberated and escapes in the tail gases.

2. Alumina

As a second raw material for this aluminium fluoride process an alumina component is needed. Best suited is an aluminium hydroxide (alumina hydrate) which is obtained e.g. with the well-known "Bayer" process, before calcination, with a content of 99 to 100 per cent $\text{Al}(\text{OH})_3$. This alumina gives a very good filtrable silicic acid.

Detailed experiments have shown that ordinary clay can also be used in the manufacture of aluminium fluoride, given suitable conditions. A raw clay having an analysis of:

SiO_2	48.2	per cent
Al_2O_3	42.2	" "
Fe_2O_3	1.8	" "
TiO_2	1.0	" "
loss on heating	4.0	" "
rest	1.8	" "

after calcination at 800°C gave a very good reactivity with a 15 p.c. fluosilicic acid.

C) The reaction giving a metastable oversaturated aluminium fluoride solution

The basis of the present process is the interesting capacity of the aluminium fluoride to form supersaturated metastable solutions. The α modification of $\text{AlF}_3 \cdot 3 \text{H}_2\text{O}$, at the beginning soluble, passes then irreversibly and slowly into the difficultly soluble β modification of the trihydrate, as the most stable hydrate of alumina fluoride between 0 to 100°C .

The preparation of the supersaturated solution of aluminium fluoride is effected by the reaction of the fluo-silicic acid with the alumina hydrate according to the schematic equation:-



The difficulties in effecting this reaction are:

- a) The reaction must proceed as far as possible in order to obtain later on, at the crystallisation of the trihydrate of the aluminium fluoride, a product low in silicic acid.
- b) The separated hydratic silicic acid must be obtained in a good filtrable form since the duration of stability of the aluminium fluoride solution is limited.
- c) The solution of aluminium fluoride must have a duration of stability, which just allows a separation of the silicic acid but which does not delay unnecessarily the subsequent crystallisation.

These conditions are completely realisable and without any difficulties, if the reaction proceeds in the appropriate manner. The dosage of the components of reaction is such that after reaction about 2 per cent by weight aluminium silico fluoride is still present in the aluminium fluoride solution, and the reaction temperature at the end of the reaction is 95 to 100°C . Under these conditions the whole reaction is terminated after about 15 minutes. The filtrability of the precipitated silicic acid is excellent. The time for separation, which is effected in a centrifugal

hydro extractor amounts per operation, wash time inclusive, to 0 to 10 minutes. The water content of the product from the extractor is about 40 per cent, and the aluminium fluoride content, which is not removable by washing, is about 5 per cent by weight. If no better use is found for this pure white silicic acid, it can be recycled into the vessel in which the superphosphate is mixed to increase the yield of fluorine.

As mentioned before it is also possible to react suitable calcined clays (instead of hydrate of alumina) with fluosilicic acid to get solutions of aluminium fluoride. The reaction is effected as described before. The earth and alkaline metals as well as the iron and titanium content of the clays, are separated at a pH value of 3.9 at 100 °C with the silicic acid, and are practically eliminated from the aluminium fluoride solution. It is a pre-condition for this separation that the iron is present within the calcinated clay in a trivalent form, which is the case with an oxidizing calcination of the raw materials.

D) The crystallisation of the trihydrate of aluminium fluoride

The solution of aluminium fluoride is metastable. If it is left to itself, then the α -aluminium fluoride trihydrate, which is with difficulty soluble, crystallises within 3 to 6 days in the form of hard incrustation. In order to get a technically usable crystallisation rate some measures are necessary, such as an addition of seeding crystals, stirring, and maintenance of a temperature of 95 °C during the crystallisation. If the solution's content of approximately 2 per cent aluminium silicofluoride, originating from the reaction, is maintained, the crystallisation time is from 3 to 5 hours. The initial concentration of the solution is of no direct influence to the crystallisation rate.

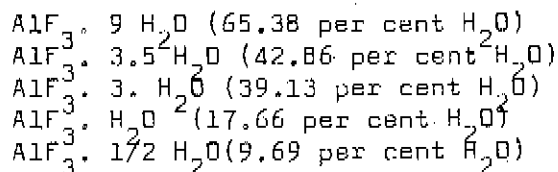
The crystallized β - aluminium fluoride trihydrate ($\text{AlF}_3 \cdot 3 \text{H}_2\text{O}$) is finely crystallised. The product of the extractor has a moisture content of 5 per cent and a water of crystallisation content of 39.1 per cent according to the formula. Impurities present in the crystals amount to less than 0.1 per cent SiO_2 ,

and less than 0.01 per cent P_2O_5 and Fe_2O_3 . A SO_3 content is no longer detectable (less than 0.03 per cent). Thus the product can meet the highest purity requirements.

7 to 10 per cent of the total aluminium fluoride remain in solution in the mother liquor. It can be used again by feeding it into the tail gas washers of the superphosphate plant. The aluminium fluoride being in solution, is transformed into aluminium silicofluoride, thus coming back again with the fluosilicic acid to be reacted and crystallized. If the content of phosphate and of iron becomes excessively high in this cycle, the mother liquor must be rejected occasionally.

E) The calcination of the aluminium fluoride trihydrate

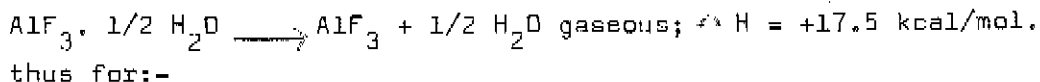
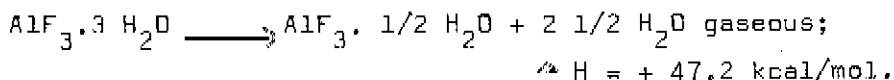
The crystallized trihydrate of aluminium fluoride which has passed through the extractor contains approximately 45 per cent of chemically bonded and free water. It is known that there are several definite hydrates of aluminium fluoride, e.g.:-



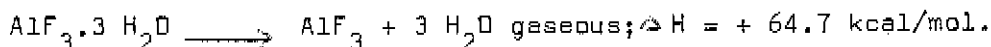
so that it is possible to plan a dehydration in stages.

Heating up the trihydrate to $180^\circ C$ there remain about 17 per cent water in the product (corresponding to $AlF_3 \cdot H_2O$), at 220° 9 per cent water (corresponding to $AlF_3 \cdot 1/2 H_2O$) and at $240^\circ C$ about 6 per cent water. Further dehydration becomes very hard, and only at $600^\circ C$ does the water content of the aluminium fluoride fall below 0.5 per cent.

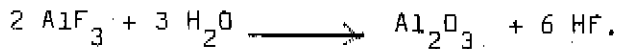
From the thermic data the heat requirements of each stage of dehydration can be calculated:-



thus for:-



A considerable amount of heat is required for the calcination to produce one metric ton of aluminium fluoride; it runs as high as about 1.15 million kcal. Beside the supply of the necessary heat, another difficulty with the dehydration of aluminium fluoride trihydrate is the decomposition connected with it, with separation of hydrofluoric acid, according to the equation:-



The technically prepared aluminium fluorides, which are practically all calcinated in kilns, show therefore an AlF_3 content of 88 to 95 per cent only. The rest is mainly Al_2O_3 beside the usual impurities. Thorough studies of the dehydration process with the trihydrate of aluminium fluoride revealed that the decomposition and the loss of the hydrofluoric acid can be practically avoided, if the hydrate is brought, preferably within one second or less, to the final temperature of the calcination. On the basis of this experience a two-level fluidised bed furnace was designed and built for the calcination of the trihydrate for technical production. On the first level the trihydrate is brought to a water content of about 6 per cent at the relatively low temperature of 240°C which is advantageous from an economic point of view. Three quarters of the whole amount of heat needed are supplied at this level by indirect heating. On the second level the product is completely dehydrated at a temperature of about 600°C to a water content of below 0.3 per cent. The product flows through both levels of the furnace with a fluidised bed by natural overflow. The finished product is finely crystalline, and can be bagged immediately after a simple air cooling.

The average analysis of the calcinated aluminium fluoride after manufacture is approximately as follows:-

AlF_3	97 to 98 per cent
SiO_2	0.1 to 0.2 per cent
P_2O_5	0.1 per cent
Fe_2O_3	0.02 per cent
SO_3	<0.05 per cent
H_2O	0.3 per cent
Al_2O_3	rest to 100 per cent

All corrosion problems existing in connection with the process could be solved by the use of alloyed steels, rubber linings, and graphite (for the heat exchanger).

The process for producing aluminium fluoride from fluosilicic acid is therefore a further contribution for better exploitation of the fluorine content of rock phosphate.

The advantages of the new process, which was developed by the Austrian Nitrogen Works Ltd. (Osterreichische Stickstoffwerke Aktiengesellschaft) in Linz on the Danube, and which has been running on a commercial scale for about one year with a capacity of 1200 metric tons a year of aluminium fluoride, consist in the following points:-

- 1 - In the simplicity of the process (no hydrofluoric acid as an intermediate product),
- 2 - In the purity of the finished product,
- 3 - In the profitability of relatively small units, from 800 metric tons production per year upwards.

In conclusion I wish to thank my collaborators, in particular Dr. Alfred Schmidt and Dr. Walter Müller, who have made an important contribution to the success of this development.

FIGURE 1

1 heat exchanger	6a,6b,6c crystallizers
2 centrifugal pump	7 centrifuge
3 H_2SiF_6 measuring vessel	8 calcination furnace
4 reactor	8a 1st stage
		8b 2nd stage
5 centrifuge	8c combustion chamber

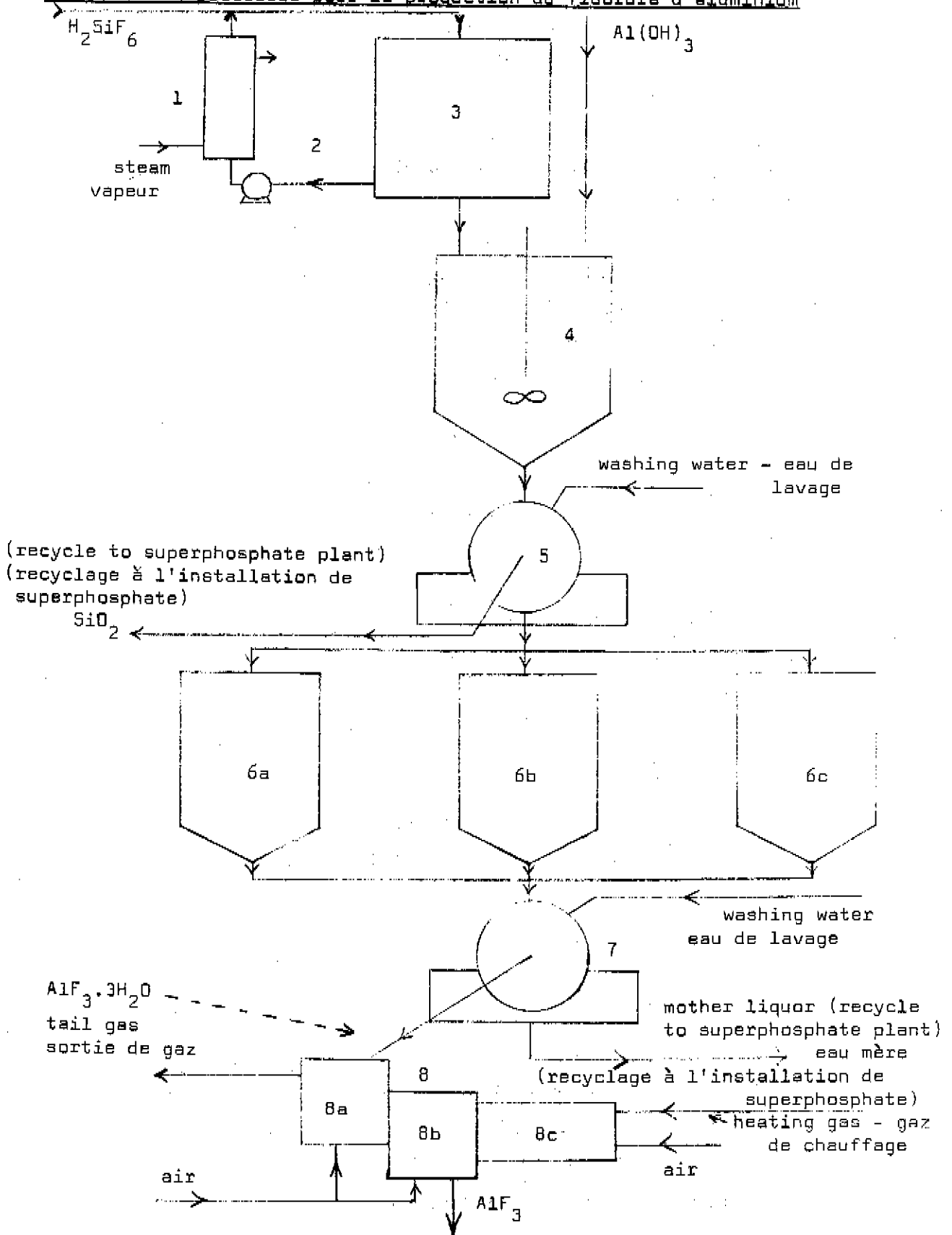
Yield on AlF_3

related to hydrate of alumina ... 85 per cent

Losses on AlF_3 by per cent:

- 5 p.c. in the hydr. silicic acid
- 7 p.c. in the mother liquor
- 3 p.c. as dust with calcination

FIGURE 1 Aluminium fluoride production process diagram
Diagramme du processus pour la production du fluorure d'aluminium



DISCUSSION

MR. F. WEINROTTER (Austria) : This paper reports a new, simple process for the production of aluminium fluoride. Fluosilicic acid and alumina hydrate are used as raw materials. The fluosilicic acid is obtained from processes using phosphate rock, such as the superphosphate process, when the evolving gases are washed with water. The usual concentration of the fluosilicic acid for aluminium fluoride production is 17% - 18%. Alumina hydrate is produced by the well-known Bayer process. Under suitable conditions of reaction between fluosilicic acid and alumina hydrate, hydrated silicic acid is precipitated and separated. Good filterability of the silicic acid is essential for the process. From the remaining unstable supersaturated aluminium fluoride solution, a stable, relatively insoluble aluminium fluoride trihydrate is crystallised. The crystalline product is very pure and easily separated from the mother liquor. The wet product contains 40% water of hydration and 5% moisture, which are removed at temperatures of 240°C and 600°C with due regard to heat economy. A newly designed, two-stage, indirectly heated furnace, using fluidised solids, is used for the calcination. The aluminium fluoride obtained is 98% pure and especially suitable for aluminium production. The new process has been operated by the Oesterreichische Stickstoffwerke A.G. at Linz for more than a year now, with good success. The present production capacity is 1200 tons/year. The direct production of aluminium fluoride from fluosilicic acid without using hydrofluoric acid offers many advantages. The process is thus economically advantageous even at production capacities of less than 1000 tons/year.

MR. P. ROUX (France) : Mr. Weinrotter has given a very clear account of a process recovering hydrofluoric acid as a by-product in superphosphate manufacture and converting it into a product with an assured market, namely aluminium fluoride, the most sought-after of all fluoride compounds. The Oesterreichische Stickstoffwerke seems to have solved the problem of economic profitability, which can be expected to be

achieved at a minimum production level of 800 tons per year of aluminium fluoride. In view of fluorine recovery yields, this minimum production level presupposes a factory which processes at least 125,000 tons of phosphate rock per year. Obviously, this factory would need to be of a considerable size.

I should like to put the following questions to the author: firstly, has Mr. Weinrotter studied the effect of the fineness of the phosphate rock on the amount of fluorine remaining in the superphosphate?

We should also like to know whether the silica obtained during manufacture can be marketed, perhaps after a fairly simple purification process; for, in this case, the profitability of the process would be improved.

Since the P_2O_5 content of the fluosilicic acid must be about 200 to 300 mg per litre, one must necessarily de-dust the gases before their entry into the scrubber. Could the author give details concerning the apparatus used for this purpose, particularly with regard to the construction material used - the specification of the stainless steel, for example?

The idea of a two-stage fluidised-bed furnace for the calcination of the aluminium fluoride trihydrate is extremely interesting for it minimises the decomposition and loss of hydrofluoric acid which accompanies the calcination of the product. The low percentage of fluorine losses in the dust is very notable. Can the author give information as to the de-dusting plant which must be used in conjunction with the fluidised-bed furnace, particularly with regard to its size?

MR. WEINROTTER : With regard to the first question, relating to the fineness of the phosphate rock used, this factor is not very important. What is important is the amount and concentration of the acid and the amount of acid recycled.

As far as marketing the silica is concerned, this does not happen because it is returned into the superphosphate manufacturing process in order to increase the fluorine yield.

With regard to the de-dusting of the gases entering the scrubber, we use a cyclone made of ordinary steel coated with

rubber. Similarly, with regard to the last question, we also use a cyclone.

Mr. N. LAGERHOLM (Sweden) : In recycling the silica which is produced and precipitated in the reaction between the hydrofluosilicic acid and the alumina hydrate, do you mix it with the rock phosphate or with the sulphuric acid in the superphosphate plant ?

Secondly, I am not quite clear regarding the water balance in your process. Water is taken into the process at several stages : you introduce washing water and at the end of the process you recycle the mother liquor to the superphosphate plant. The diagram seems to indicate a build-up of water through the whole process. Could you say at what point it is taken out ?

Mr. WEINROTTER : With regard to the first question, the silica is recycled during the superphosphate manufacturing process itself, and is thus put back into the mixture of sulphuric acid and phosphate rock.

The answer to the second question is that the water is removed with the silicic acid.

Dr. K. C. SCHEEL (Germany) : The hydrofluosilicic acid produced in the superphosphate plant usually has a small content of phosphoric acid. Does this phosphoric acid do any harm in this process?

Mr. WEINROTTER : This phosphoric acid remains during the course of the crystallisation of the mother liquor.

Mr. N. D. GOPINATH (India) : Will Mr. Weinrotter indicate the type of filter and filter cloth, and the life of the cloth, which has been used to filter this aluminium fluoride? Secondly, what type of crystalliser is used to crystallise the aluminium fluoride?

Mr. WEINROTTER : The filter is a centrifuge. The crystalliser is a den with a mixer.

Mr. NOUYRIGAT : In view of certain incalculable factors, particularly from the point of view of the filtration of the silica precipitated during the first phase of the process, could the author indicate what is the order of magnitude of

the investment required by this process for a throughput of 100 kg/hour of fluorine ?

Mr. WEINROTTER : The cost of a plant producing 1,200 tons of aluminium fluoride per year is 4 million Austrian Schillings.

Mr. UUSITALO : You show in your paper, that, depending on the reaction conditions and the origin of the rock phosphate, only 12% of the fluorine content of the rock phosphate can be obtained in tail gas, the remainder staying in the superphosphate. After that you state that, using all possibilities, you are able to increase the yield of fluorine by two to three times. What are these possibilities you use, and do you really think the maximum fluorine yield is as small as 24% - 36% ?

Secondly, are you using the same centrifugal hydroextractor for filtering silicic acid and aluminium fluoride ?

Mr. WEINROTTER : With regard to the first point, the possibilities I am referring to involve a small increase in the sulphuric acid concentration and the reaction temperature, and also the amount of acid used. All these factors increase the yield of fluosilicic acid. Particularly effective when working with a rock phosphate poor in silicic acid is an addition of rock phosphate rich in silicic acid or of hydrated silicic acid, as it is obtained in the manufacture of aluminium fluoride.

Concerning the second question, we use two extractors - one for the silicic acid and one for the aluminium fluoride.

Mr. A. C. VAN ES (Netherlands) : You say you remove the silica by means of a centrifuge. Do you mean a separator or a real centrifuge ?

Secondly, you say that your aluminium fluoride is finely crystallised. As far as I understand, this product is used in the aluminium industry, which is, I think, interested in having a fairly coarse aluminium fluoride in order to prevent losses in the electrolysis.. Have you considered crystallising in forms other than at present, or introducing more aluminium fluoride into your crystalliser ?

Mr. WEINROTTER : We use a real, closed centrifuge. The

crystals are used in the form they assume at the outlet of the crystalliser, with a size range of 30 - 50 μ . This is a normal size range for the aluminium industry. Other products on the market have the same dimensions.
