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FLUORINE RECOVERY IN THE PHOSPHATICFERTILISER INDUSTRY

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FOREWORD

This paper deals with certain aspects of the recovery of fluorine from the phosphatic fertiliser industry, and essentially describes processes developed by the authors for the winning of waste fluorine of the industry as alkali silicofluoride and its subsequent conversion into sodium fluoride of technical grade, chemically pure sodium fluoride, synthetic cryolite, aluminium fluoride, etc. Process details have not been given elaborately since Patent claims have been registered for some of the processes described.

These processes were developed, experimented in pilot plants and put into semi-commercial operation within a comparatively short period of three years from 1965 to 1967. We were able to achieve this only because of the vision, leadership, guidance, unfailing support and personal interest of Mr. M.K.K. Nayar, our Managing Director, who has made significant contributions to the development of the Fertiliser Industry in India. We shall be failing in our duty if we do not place on record here, our deep sense of gratitude to Mr. M.K.K. Nayar personally and to M/s. Fertilisers and Chemicals, Travancore Limited, in general, for all the valuable assistance we have received in our task.

INTRODUCTION

At present, almost all of India's requirements of fluorine chemicals are met by imports. The scarcity of high grade fluorspar deposits in the country is probably the reason for these imports which run to the amount of more than Rs. 20 million currently, and are expected to be of the order of about Rs. 6 million by the year 1971. Since the country imports about 1 million tonnes of rock

phosphate annually, carrying with it about 40,000 tonnes of fluorine which, incidentally, reaches us free of duty and cost, and since all of this fluorine is wasted, either in the fertiliser or as a waste effluent of the fertiliser industry, it was considered as a worthwhile potential raw material for the manufacture of fluorine chemicals. It has been estimated that if the fluorine content of the wet-process phosphoric acid which is now made in five major factories in India could be recovered, this alone could make India a surplus producer of fluorine chemicals. Sufficient technical know-how has been indigenously developed by the Research Division of FACT to warrant the installation of fluorine-recovery plants as adjuncts to all the phosphatic fertiliser units in and outside the country which have evinced keen interest in the matter.

GENERAL

Commercial grades of rock phosphate used in the manufacture of wet-process phosphoric acid contain 3.75 to 4.5% by weight of fluorine. 45% to 60% of this is retained in the wet-process acid of 30% P_2O_5 strength, as hydrofluorosilicic acid. Silicon tetrafluoride and hydrogen fluoride are also present in equilibrium with hydrofluorosilicic acid. The fluorine contents of different grades of rock phosphate commonly used in fertiliser manufacture, as well as in the product acid from them, are given in Table 1.

TABLE I

No	Type of rock	Fluorine in rock	Fluorine in 30% P_2O_5 Acid
1	Morocco	4.4	1.70
2	Jordan	4.05	1.18
3	Gafsa	4.17	1.40
4	Safaga	3.75	2.20
5	Florida	4.10	2.70
6	Togo	3.90	2.40

It has been observed that the fluorine content of wet-process phosphoric acid varies with several factors such as :

- (a) the quality of the rock phosphate used;
- (b) the concentration of the product acid;
- (c) the strength of the sulphuric acid employed in the process;
- (d) the temperature of the reaction;

but the quantitative relationships between them have not been investigated.

Recovery of fluorine by the proposed process described below, not only yields valuable fluorine chemicals, but also much reduces the operating problem associated with the concentration of wet - process phosphoric acid. In addition it helps eliminate several of the difficulties encountered in the subsequent production of phosphatic fertilisers and chemicals.

MANUFACTURE OF SODIUM SILICOFLUORIDE

When a soluble sodium salt is added to phosphoric acid containing fluosilicic acid, the sparingly soluble silicofluoride is precipitated. It may be seen from Graph I, that the solubility of sodium silicofluoride in water at 30°C is 0.925, while that in 30% P₂O₅ acid at 30°C is 0.44.

CHOICE OF SODIUM SALT

Several of the commercially available sodium salts have been tried, and we have found that technical grade trisodium phosphate (if available - as in our case) is most suitable.

The cheapest sodium salt, namely sodium chloride, is not recommended, since it introduces chloride ions into phosphoric acid, which would create corrosion problems in the plant for subsequent operations. Cost considerations exclude the use of caustic soda, while soda ash creates frothing troubles. Sodium sulphate from viscose rayon plants can be used if available economically, if the phosphoric acid is subsequently to be used for Ammonium Phosphate-Sulphate manufacture, since the soluble product of the reaction is sulphuric acid which anyway has to be added subsequently.

PROCESS

(See Flow Sheet I). Wet-process acid coming from the clarifier contains approximately 0.1% suspended matter. The removal of this is absolutely essential in order to obtain pure sodium silicofluoride. Thus, the acid is filtered through filter presses, using nylon or similar cloth, and the clear acid is then fed to a reactor. In this vessel, calculated amounts of trisodium phosphate are added with proper agitation. Rubber-lined M.S. vessels are used for this. Sufficient time is allowed for the reaction to proceed to completion, after which the slurry is fed to a settling tank. Supernatant phosphoric acid is sent to the storage tanks while the thick slurry at the bottom is filtered and washed free of soluble P₂O₅.

The analysis of the defluorinated acid is given in Table II, and that of the sodium silicofluoride produced in Table III.

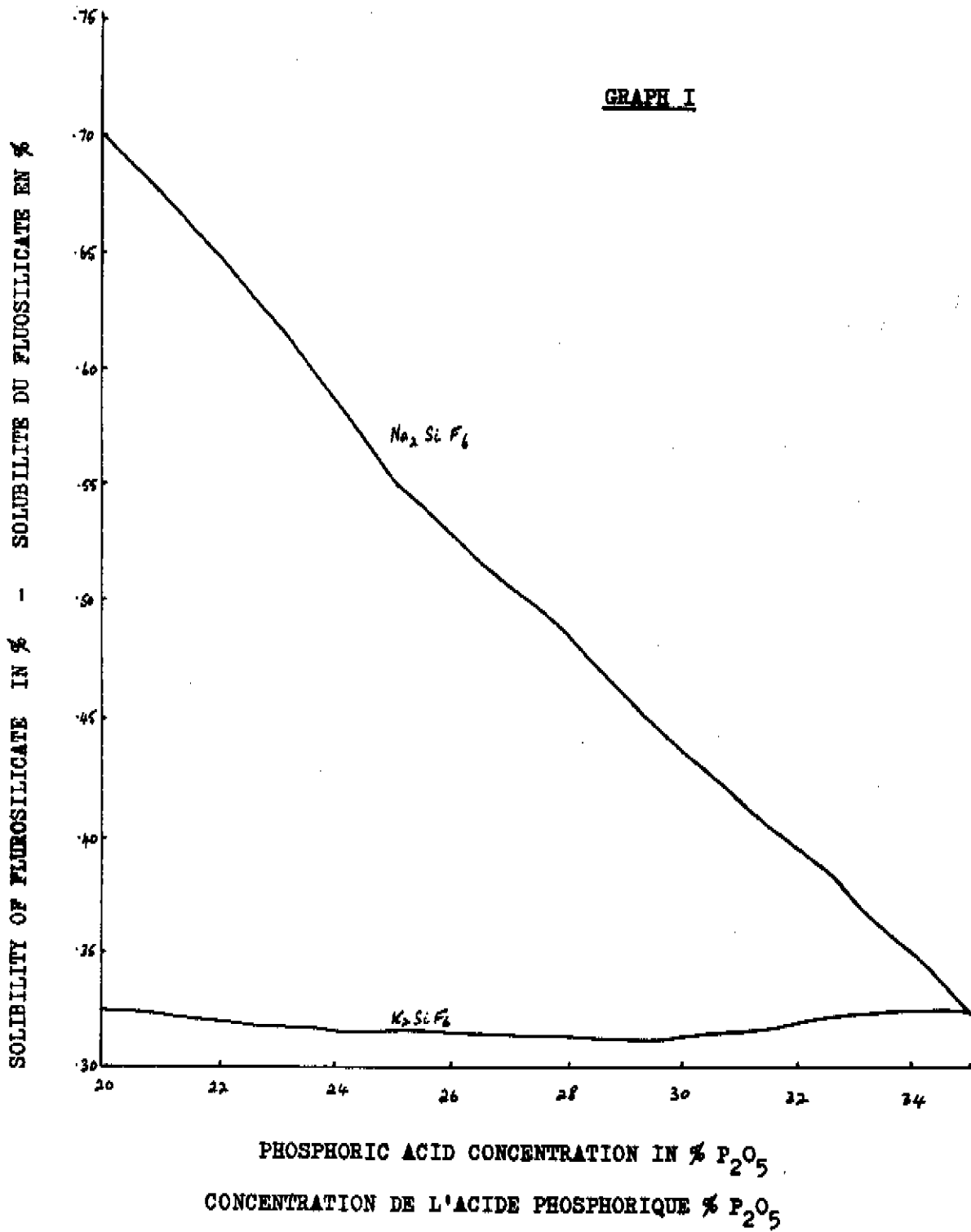
The yield per tonne of P₂O₅ is 60 - 70 Kgs of sodium silicofluoride.

TABLE IIANALYSIS OF THE DEFLUORINATED ACID

	Initial concentration P_2O_5 in phosphoric acid	Fluorine content in the acid	Final concentration P_2O_5 in phosphoric acid	Fluorine content in the treated acid
1	30. 0 %	2. 01 %	30. 4%	0.15% (without washing)
2	28. 0 %	1. 98 %	27. 1%	0.16% (with washing)
3	29. 0 %	1. 99 %	26. 4%	0.165% -do-
4	26. 01 %	1. 91 %	24. 6%	0.158% -do-

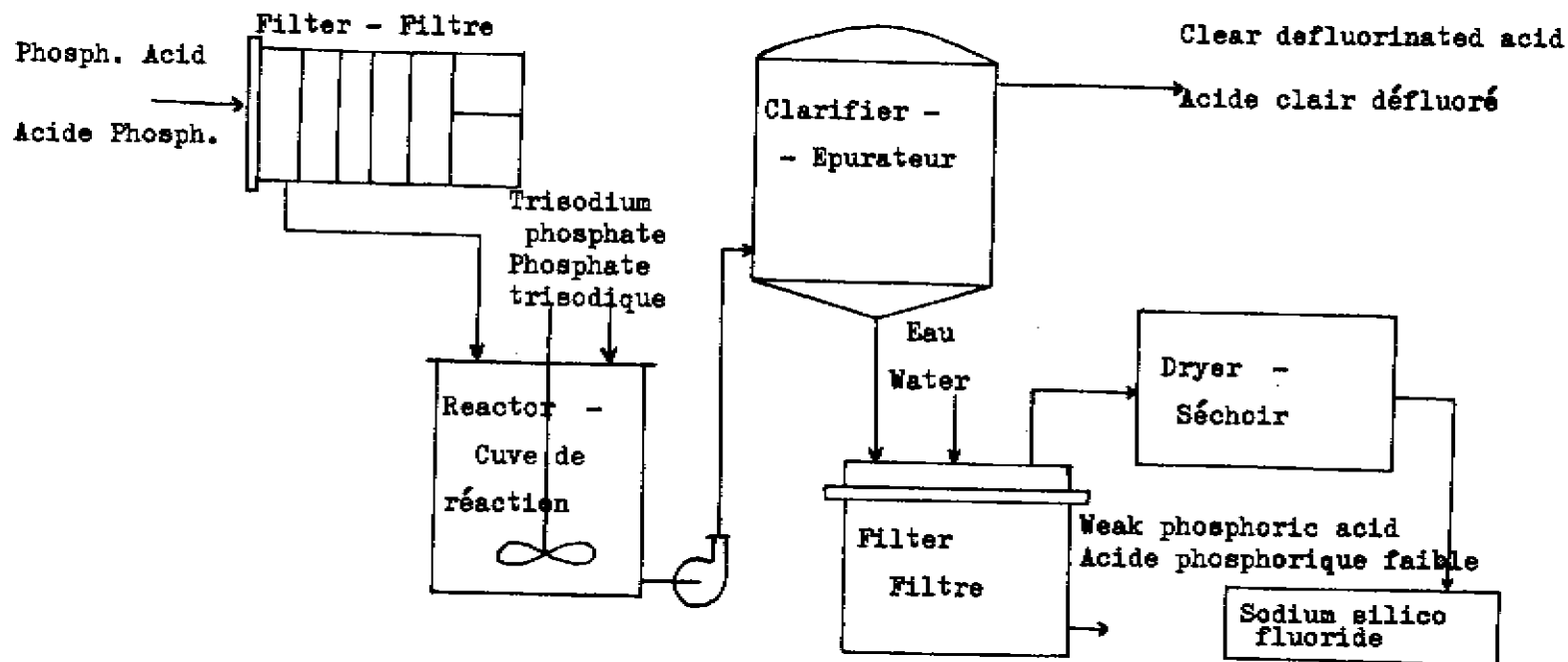
TABLE IIIANALYSIS OF SODIUM SILICOFLUORIDE

Assay	..	98.39 %
P_2O_5	..	0.25 %
CaO	..	0.28 %
SO_4	..	0.08 %
Moisture	..	0.5 %
Water insoluble	..	0.04 %
Fe_2O_3	..	0.004%
Al_2O_3	..	0.003%
Sieve	100%	through 200 mesh.

GRAPH I

FLOW SHEET I

FLUOSILICATE DE SODIUM -
- SODIUM SILICO FLUORIDE

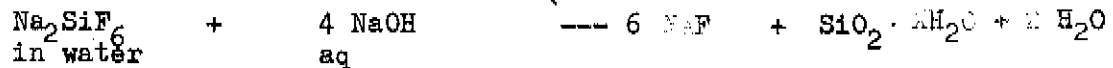


MANUFACTURE OF TECHNICAL GRADE SODIUM FLUORIDE.PRINCIPLE

When sodium silicofluoride is added to sodium hydroxide solution and heated, the silicofluoride ion is decomposed, producing sodium fluoride and hydrated silicon dioxide. In the presence of excess alkali the silica is dissolved in the free alkali and forms a solution of sodium silicate. The crystals of sodium fluoride may thus be separated from the silica.

PROCESS: (See Flow Sheet II)

Sodium silicofluoride is made into slurry of about 30% strength in water and heated to 80-85°C in a stainless steel vessel with steam jacket. To this a thin stream of 40% caustic soda lye is added with good agitation. The reaction is exothermic and the temperature rises to over 100°C. The reaction may be represented by:



A minimum excess of alkali than is indicated by the equation is also added and the reaction allowed to proceed to completion by stirring for half an hour. The reaction slurry is cooled to room temperature by letting in cold water to the jacket, and filtered. The crystals of NaF are washed with cold water and dried in an electrically heated dryer. The product analysis is given in Table IV.

TABLE IVANALYSIS OF TECHNICAL GRADE SODIUM FLUORIDE

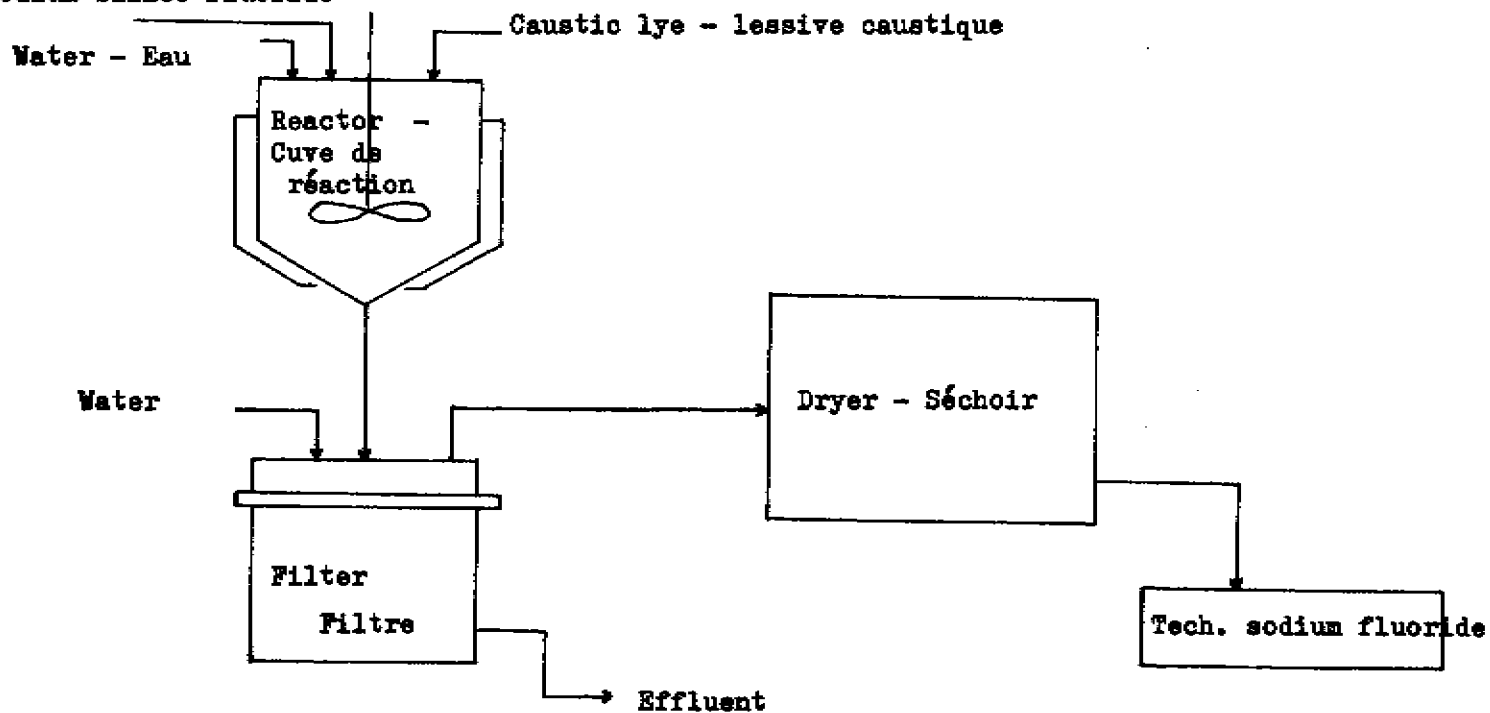
Assay	..	98 % (Min.)
Insolubles	..	0.2 to 0.3%
P ₂ O ₅	..	Less than 0.2 %
CaO	..	Less than 0.1 %
SiO ₂	..	0.5 to 0.6%
SO ₄	..	nil
Cl	..	nil
Fe ₂ O ₃	..	nil
Al ₂ O ₃	..	nil
Moisture	..	0.05 to 0.1 %

FLOW SHEET II

TECHNICAL GRADE SODIUM FLUORIDE - FLUORIDE DE SODIUM DE TITRE TECHNIQUE

Fluosilicate de sodium

Sodium silico fluoride



MANUFACTURE OF HYDRATED CALCIUM SILICATEPRINCIPLE

The effluent sodium silicate solution is impure and cannot be employed as such for any process. Thus, it is neutralised by passing through CO_2 gas at an elevated temperature to precipitate hydrated silica. This is filtered and washed. The sodium carbonate solution is then causticised with lime by which means all fluorine impurities are removed and reasonably pure sodium hydroxide solution obtained. In this, the silica is dissolved and then converted to special grade hydrated calcium silicate.

PROCESS (See Flow Sheet III)

Impure sodium silicate solution from the sodium fluoride plant is taken into a wooden tank and heated by open steam to $60 - 65^\circ\text{C}$. Carbon dioxide gas is then bubbled in through specially designed bubblers, using booster pumps. When the precipitation of silica is complete, the slurry is subjected to filtration. The filtrate is sent to the causticising unit while the silica is washed with water.

The sodium hydroxide solution obtained as filtered from causticising is pumped to a digester tank where it is heated to about 75°C . by open steam and agitated. The silica from the previous operation is then fed in gradually until all the silica is dissolved. The solution is pumped at a controlled rate to another tank in which calculated amounts of hydrochloric acid of about 8% strength is taken and kept stirred. The silica solution is then prepared and pumped into another tank, in which an approximately 5% lime slurry sieved through 200 mesh sieve, is kept at about 80° with good agitation. The concentration of the reactants, pH, temperature and time of reaction etc. are critical. The reaction is allowed to take place in the course of 75 - 80 minutes, after which the slurry is filtered in Nutsch filters, washed several times with water and dried at 200°C .

The analysis of the product is given in Table V.

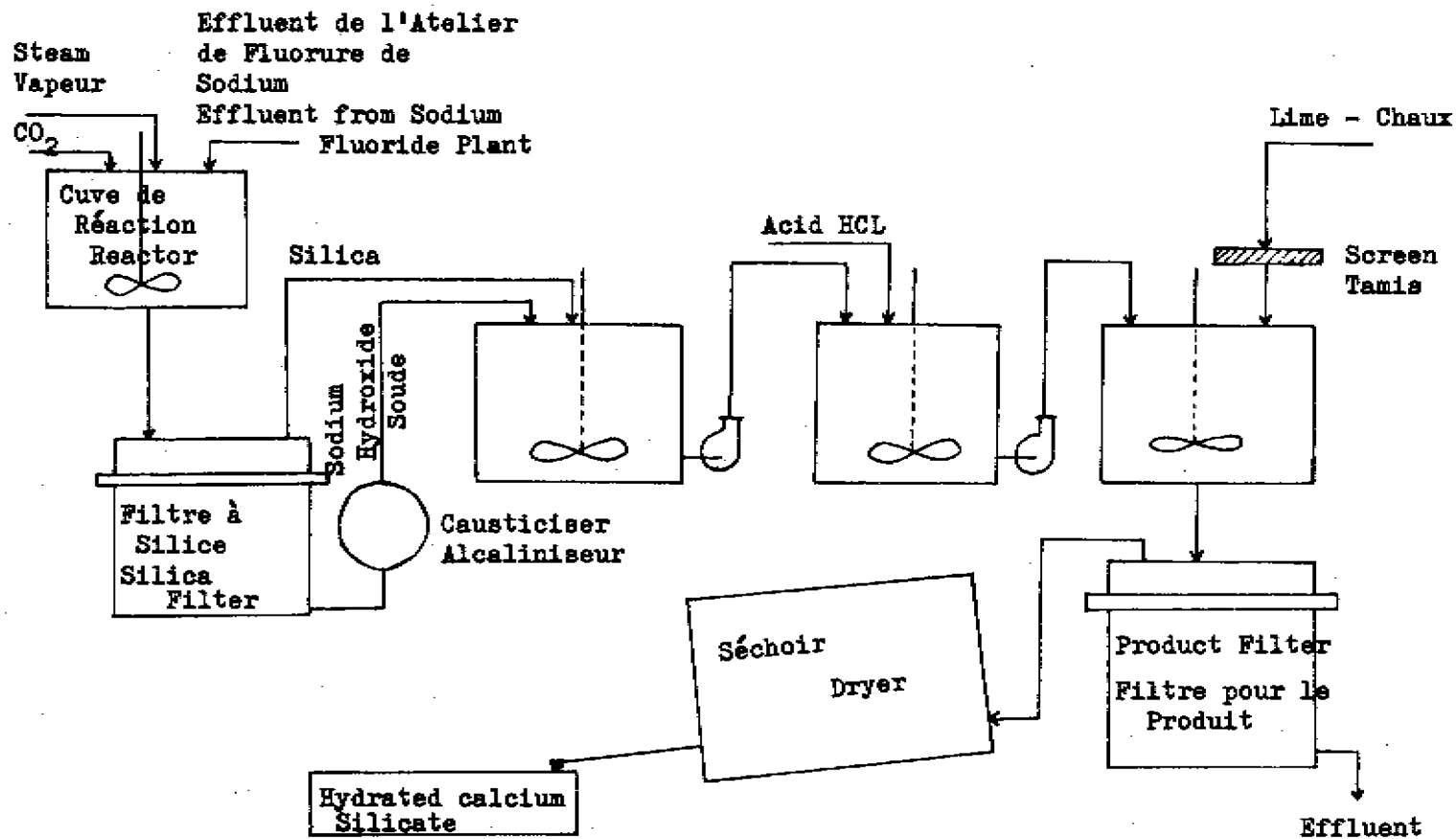
TABLE V
ANALYSIS OF HYDRATED CALCIUM SILICATE

Bulk density	..	0.07 to 0.08
Oil absorption	..	600%
Sieve analysis	..	99.5% to 300 mesh
CaO	..	16 to 18%
SiO_2	..	68 to 70%
Water	..	10 to 12%

FLOW SHEET III

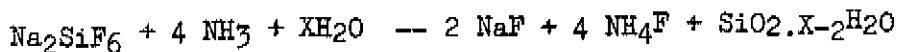
HYDRATED CALCIUM SILICATE

SILICATE DE CALCIUM HYDRATE

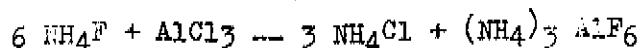
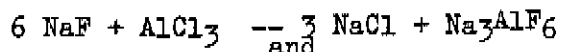


MANUFACTURE OF SYNTHETIC CRYOLITEPRINCIPLE

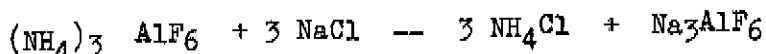
Ammonia reacts with sodium silicofluoride as per the equation:



When the silica is filtered off and the mixed solution of sodium fluoride and ammonium fluoride is treated with an aluminium salt, the following reactions take place:



The resultant slurry of sodium and ammonium cryolite is then reacted with sodium chloride, when the ammonia in $(\text{NH}_4)_3\text{AlF}_6$ is replaced by a sodium ion and a slurry of Na cryolite obtained.

PROCESS (See Flow Sheet IV)

Sodium silicofluoride and water are mixed in a slurry preparation tank to obtain a 25% slurry. This is pumped into a specially designed reactor into which ammonia gas is injected. When a pH of 9 - 9.5 is reached in the reaction mixture, ammonia injection is stopped and sufficient retention time is allowed for the completion of the reaction. The slurry is then diluted with calculated amounts of water in a fluoride digestion tank, and cooled. It is filtered and the silica washed with water to recover all possible fluorides. The filtrate is pumped into the cryolite reactor to which the necessary volume of dilute aluminium solution is added. The temperature is kept at about 80°C and the addition is made in the course of about half an hour. This slurry is then added to the second cryolite reactor where sodium chloride solution is made to react with ammonium cryolite, forming sodium cryolite. This reaction is complete in about half an hour, after which the sodium cryolite crystals are filtered in cloth filters under vacuum, washed free of soluble salts, dried at 150°C. and calcined at around 450°C.

By controlled ammoniation of sodium silicofluoride it has been possible to obtain a highly filterable form of hydrated silica which can be washed well. The filtrate under optimum conditions is practically free from silica. So also, it has been found that cryolite obtained by metathesis of ammonium cryolite is more filterable than any other type made by direct action of sodium salts and aluminium salts.

The settling characteristics of synthetic cryolite are given in Table VI.

TABLE VISETTLING CHARACTERISTICS OF SYNTHETIC CRYOLITE

Length of slurry column : 10"

Time in minutes	Height of clear liquor layer.
0	0.00
1	0.70
2	1.35
3	1.95
4	2.50
5	3.10
6	3.50
7	3.95
8	4.30
9	4.70
10	5.00
15	6.50
20	7.15
25	7.55
30	7.90
35	8.10
16 hours	9.00

A typical analysis of cryolite obtained by this method is given in Table VII.

TABLE VII
ANALYSIS OF CRYOLITE

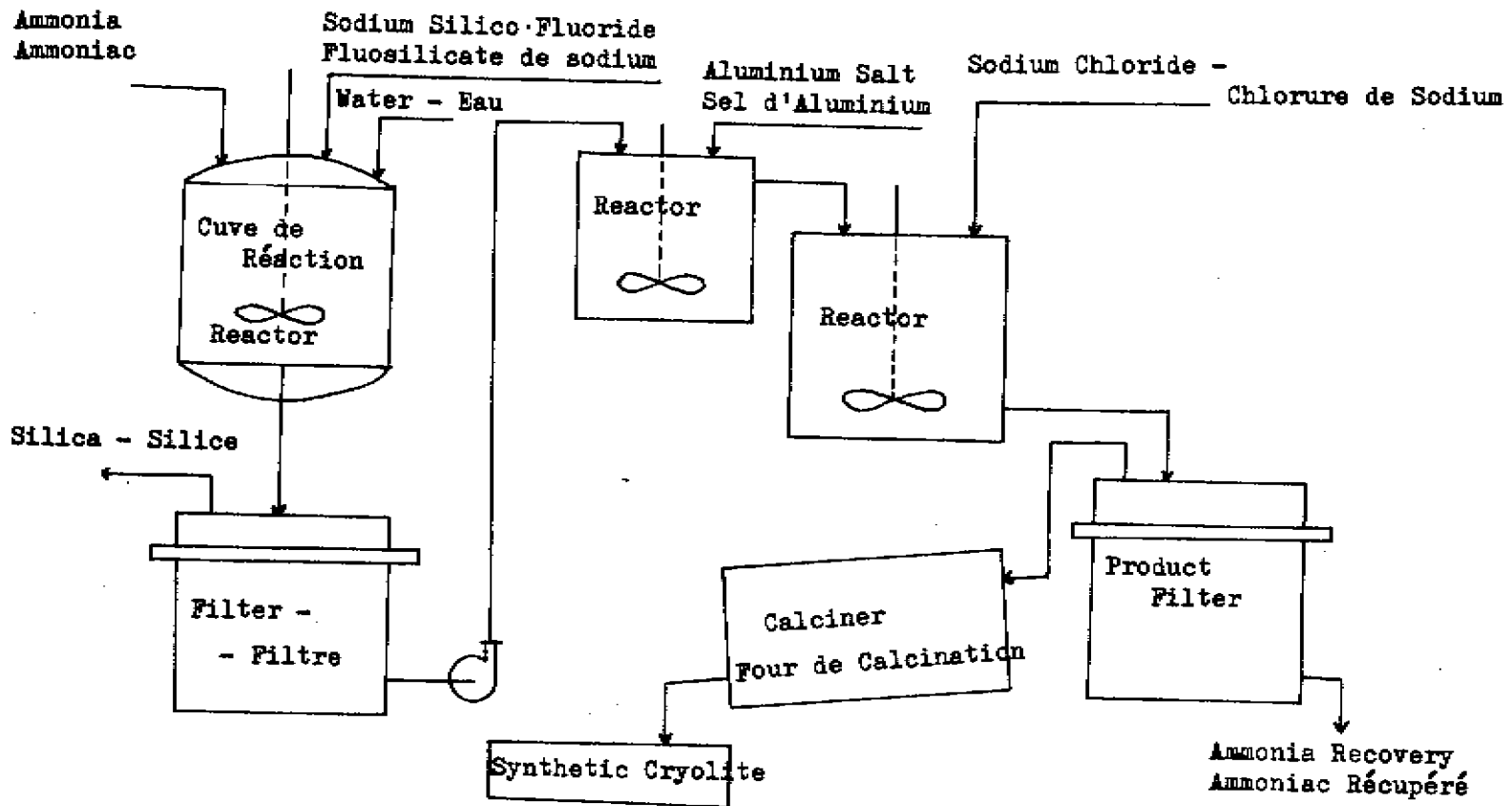
Assay	..	98.0%
Fluorine	..	53.6%
Aluminium	..	13.9%
Silica	..	0.3 to 0.6%
Sulphate	..	Traces
Chlorides	..	Traces
Fe ₂ O ₃	..	Traces
Sieve	..	97.5% - 300 mesh
Bulk density	..	006

The above method has also been adopted to the manufacture of cryolite from hydrofluosilicic acid obtained by scrubbing the den gases of the superphosphate plants.

FLOW SHEET IV

CRYOLITE DE SYNTHESE

SYNTHETIC CRYOLITE



MANUFACTURE OF CHEMICALLY PURE SODIUM FLUORIDECHEMISTRY OF THE PROCESS (See Flow Sheet V)

Addition of a potassium salt to wet process phosphoric acid containing hydrofluosilicic acid, results in the formation of the sparingly soluble potassium silicofluoride. Solubility of potassium silicofluoride is given in Graph I.

Potassium silicofluoride is decomposed by potassium carbonate solution.



The silica is filtered off and the solution of KF is treated with sodium carbonate, when



The generated K_2CO_3 is recycled in the two previous operations with required make - up.

PROCESS

Clarified wet-process phosphoric acid is treated with a strong solution of potassium carbonate containing calculated amounts of the compound. A defoaming agent is added to prevent frothing. The precipitated K_2SiF_6 is filtered and washed well. It is made into a slurry in water and pumped into a stainless steel reaction vessel, with steam jacket. The slurry is heated to 80 - 85°C, and a stream of potassium carbonate solution is fed in such a way that the exothermic reaction is made to take place at a controlled rate. When the reaction is complete, the thick slurry is cooled to room temperature, and the silica filtered and washed. The filtrate and wash water together is such that an approximately 40% solution of KF is obtained. This solution is transferred into another stainless steel reactor to which a strong solution of sodium carbonate (Theoretical amount) is fed in, with good agitation. After half-an-hour, the product is filtered and washed with minimum water to get rid of free alkali, and dried.

The analysis of this product is as given in Table VIII.

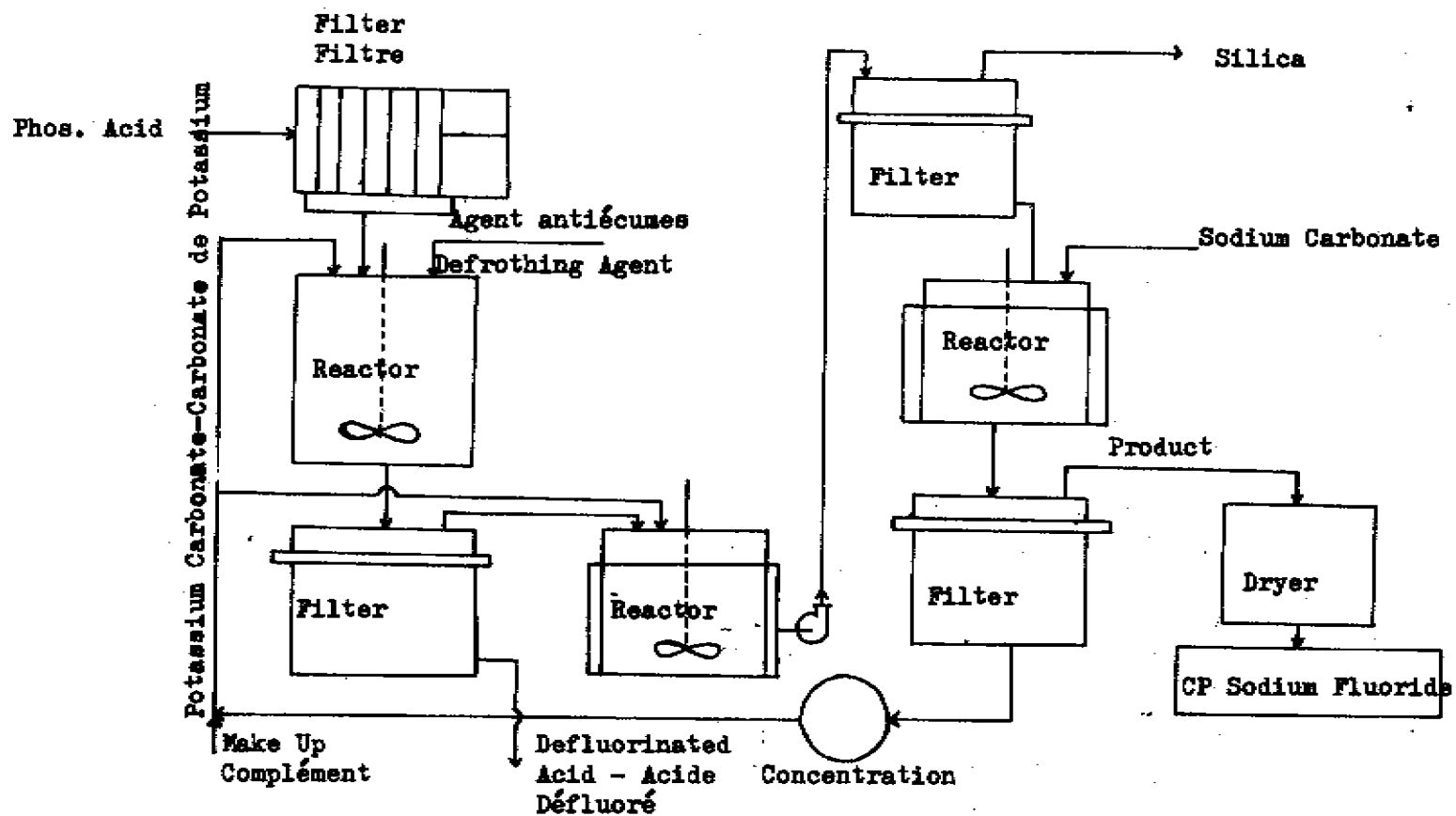
TABLE VIIIANALYSIS OF CHEMICALLY PURE SODIUMFLUORIDE

Assay Min.	..99.73%
Insolubles	.. 0.0002 %
P ₂ O ₅	.. Nil
CaO	.. Nil
SiO ₂	.. 0.0003 %
So ₄	.. Nil
Cl	.. Nil
Moisture	.. 0.05-0.1 %

FLOW SHEET V

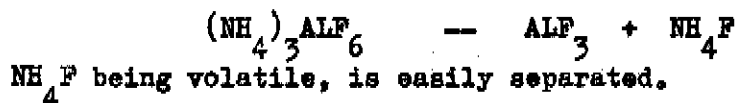
CHEMICALLY PURE SODIUM FLUORIDE

FLUORURE DE SODIUM CHIMIQUEMENT PUR



MANUFACTURE OF ALUMINIUM FLUORIDEPRINCIPLE OF THE PROCESS (See Flow Sheet VI)

Thermal decomposition of ammonium cryolite is the basis for this process.



The very low solubility of sodium fluoride in strong ammonium fluoride solution makes it possible to obtain a relatively pure solution of ammonium fluoride by ammoniation of sodium silico-fluoride. The conditions of this reaction are practically the same as mentioned earlier in the process description of cryolite, with the difference that, in this case, the slurry of sodium silicofluoride taken for ammoniation is over 50% in strength. The filter cake is washed with enough water to dissolve out all possible fluorides, collected separately and pumped to the cryolite plant.

In practice the ammonium fluoride solution contains 40% NH_4F and less than 0.3% NaF . This sodium fluoride is subsequently converted to cryolite and appears as such in the product: aluminium fluoride. But, since aluminium fluoride is used in the aluminium industry in common with cryolite, this small amount of cryolite in aluminium fluoride is tolerable and not considered as impurity.

The approximately 40% solution of ammonium fluoride is pumped to a stainless steel vessel with steam-jacket and heated to 80°C. Calculated amounts of aluminium chloride are added slowly, as a solution with agitation. After 20 minutes reaction and subsequent cooling, the slurry is filtered and the cake of ammonium cryolite washed in minimum cold water to remove soluble chlorides. The washed product is fed into a horizontal stainless steel Calciner of tubular shape, kept above 500°C. The gases evolved are scrubbed in cold water and the concentrated solution containing practically 50% of the original fluoride, is recycled to the pre-precipitation stage of the process. The calcined product, aluminium fluoride, is collected, and marketed.

The typical product analysis is given in Table IX.

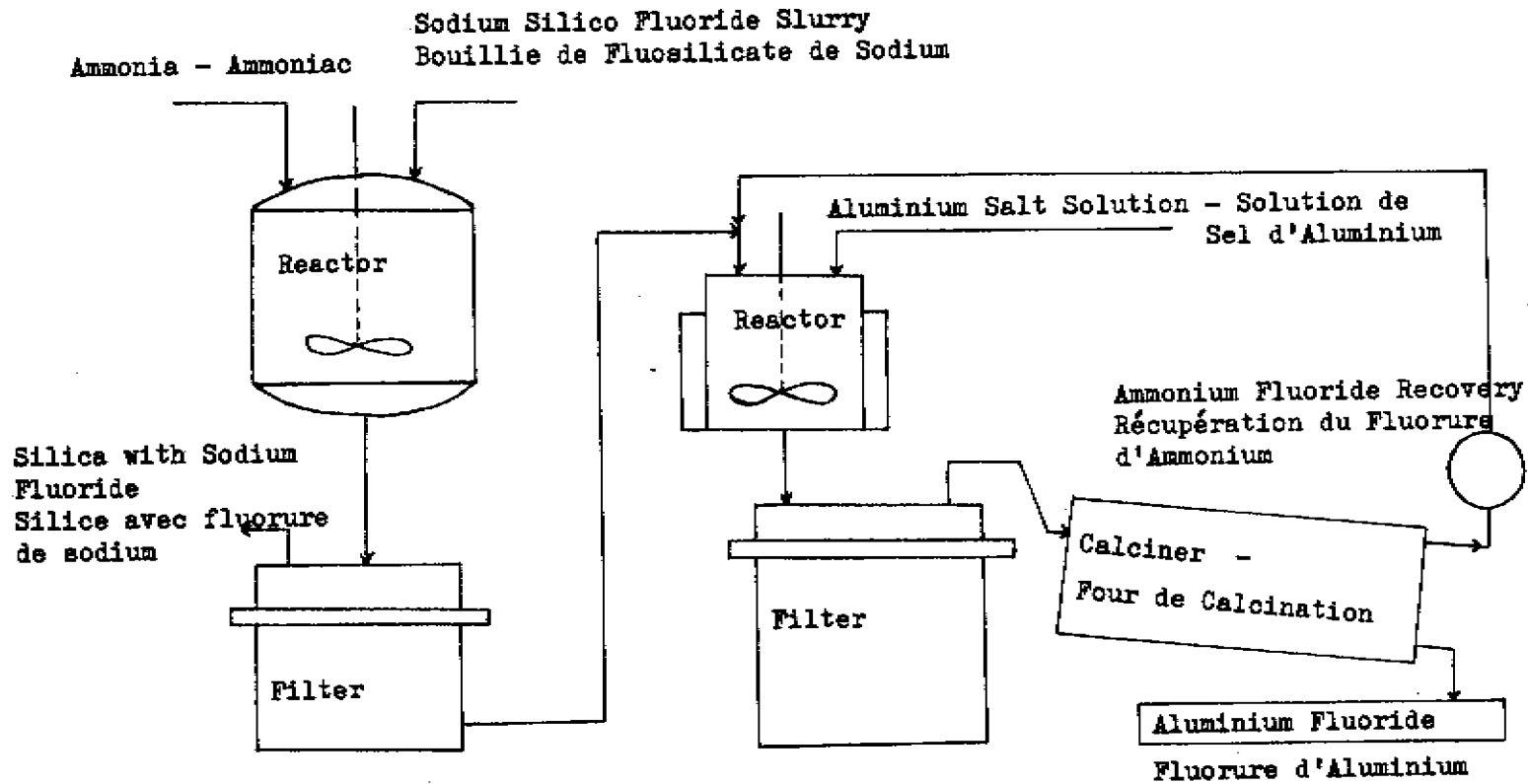
T A B L E IXANALYSIS OF ALUMINIUM
FLUORIDE

Aluminium fluoride	..	99%
Sodium cryolite	..	0.6%
SO ₄	..	Traces
P ₂ O ₅	..	Traces
Moisture	..	0.1 - 0.2%

FLOW SHEET VI

ALUMINIUM FLUORIDE

FLUORURE D'ALUMINIUM



DISCUSSION

MR. POTHEN (FACT, India): I am privileged to present to you this paper on behalf of my Company, The Fertilisers and Chemicals Travancore Ltd., with my colleague Dr. Nair. This paper has been appropriately placed at the very end of the programme because to the average fertiliser manufacturer, fluorine is an unwelcome but unavoidable product. India is deficient in natural fluoride ores and is also a great importer of very large quantities of rock phosphate. It also has a large and growing aluminium industry which imports cryolite worth about Rs 2 million/annum currently. With the growth of the aluminium industry we expect that this import bill will go up to 6 million in about 3 to 4 years. The impulse for the work, which is partly reported in this paper, came from this combination of circumstances. To some extent it was also urged on by the possible advantages which we think will accrue in the concentration step for the processed phosphoric acid if impurities represented by fluoride are removed. So this work on concentration has not been reported here and I am not yet in a position to discuss this. We believe we have a unique process for concentration. Dr. Nair and his research team took up the fluoride study under these circumstances and came up with the compendium of products and processes discussed in this paper.

Of the fluorine content in rock phosphate which is unlocked in the acidulation step about 60% is released in the gaseous effluent and about 40% stays in the phosphoric acid. When we worked out the processes based on the fluorine content in the acid, we also did supplementary work on the gaseous effluents and the processes described are equally applicable. The first step in all these processes is to precipitate the fluorine in the form of sodium silicofluoride from its original form as hydrofluosilicic acid. A variety of sodium salts as well as caustic soda have been used in this step. About 90% of the fluorine is precipitated. The presettling and the sodium silicofluoride precipitation are considered a very desirable step prior to the concentration of phosphoric acid. Starting from the sodium silicofluoride and utilizing the processes described in the paper, all of which have simple flowsheets which are also given in the paper, we have developed methods for making sodium fluoride technical grade, sodium fluoride chemical grade, cryolite and aluminium fluoride. The former two have comparatively limited markets but cryolite and aluminium fluoride have great commercial potential for India, especially in view of the rapid growth of the aluminium industry. We built pilot-plants making small quantities of sodium silicofluoride and sodium fluoride. A unique situation developed where we had customers so dependent on the output of these small plants that we have been unable to retire them from production. We were perhaps more fortunate with the cryolite in that the pilot-plant has merely created an interest in potential customers and was simply unequal to the demand. We are therefore currently building a plant which will make about 5 tons of cryolite/day but with the possibility of increasing the capacity later. By close control of conditions we have been able to consistently make a cryolite which would meet the stringent silica tolerance of the aluminium industry. We understand that the American standard allows up to 0.6% silica whereas the Indian aluminium industry demands 0.2% and perhaps even lower if they can get it. This is largely due to the emphasis on electrolytic grade aluminium, which requires a very small content of silica. As so often happens in the chemical industry the fashion in a very useful product from a by-product results sometimes in another by-product. In our case this has been very clearly demonstrated by a process for the utilisation of by-product gypsum to make ammonium sulphate which was described in an ISMA Conference in Helsinki a few years ago. We have successfully practised this for about 8 years now but we have been left with a huge

accumulation of calcium carbonate for which we have now to find a use. Similarly in this process also we have created a product which is rather a by-product left over from the making of sodium fluoride. This is sodium silicate. So we are wondering what to do with the sodium silicate. We looked round and we found a neighbouring factory which has a demand for hydrated calcium silicate, so we have also converted this and we have a small plant operating which just meets the requirement of our neighbour. The material has a tremendous absorption capacity and we have established that if we add as much as 0.1% to caking materials like ammonium chloride they remain free flowing for quite some time. We have done this type of work sometimes by force of circumstances also but we think that this hydrated calcium silicate may have a future as an anti-caking agent in the fertiliser industry.

DR. K. KARBE (Guano-Werke A.G., Germany): The authors describe the recovery of fluorine from the production of phosphoric acid 30% P_2O_5 . It is interesting that it seems possible to gain by this method all the fluorine needed in India, which until now is imported with considerable costs.

The problem of fluorine recovery is not a new one. In many factories producing superphosphate or concentrating phosphoric acid of 30% P_2O_5 we find the recovery of fluorine in the form of fluosilicic acid with a concentration up to 25 - 30%. This recovery is carried out not only to yield fluorine compounds as valuable by-products. In many cases, it is necessary to proceed in this way to avoid contamination of the air or the water. The fluosilicic acid may be transformed into the various types of silicofluorides, these salts being obtained in a very pure form, while the sodium silicofluoride gained by the process of the authors is not so pure, as is to be seen from the figures in the paper.

Of course, it is possible to transform the sodium silicofluoride gained from fluosilicic acid also into other products such as sodium fluoride, cryolite etc., and these are discussed in the paper.

Perhaps it is interesting to mention, that in our plant the step of concentration of phosphoric acid from 30% to 55% P_2O_5 yields more or less 45 kg fluorine per ton P_2O_5 in the form of a 25% fluosilicic acid. This amount may be increased under favourable circumstances to 70 kg per ton P_2O_5 .

For the precipitation of sodium silicofluoride we find in the paper an output of 60 - 70 kg per ton P_2O_5 , this value being nearly of the same order as the recovery of fluosilicic acid by the concentration of phosphoric acid.

The direct precipitation of sodium silicofluoride seems to be easier and more convenient than the two steps of absorption of the hydrofluosilicic acid and its neutralisation. In practice the precipitation of sodium silicofluoride has to take place under controlled and rather limited conditions. It is not too easy to gain a well crystallized product which can be easily separated. In our factory we precipitate silicofluoride with caustic sodium or sodium carbonate for the purification, i.e. for the defluorination of phosphoric acid. So we know well the difficulties of this operation.

There is another difficulty: the solubility of gypsum with silicofluoride. The phosphoric acid is obtained due to its special production conditions at a higher temperature. It is saturated by gypsum. There is a

tendency to supersaturation and even after cooling it takes a considerable time till the gypsum can be separated by filtration.

So the precipitated sodium silicofluoride may be more or less contaminated by gypsum. According to our experience the product gained by the authors is very good and pure according to the figures given on page 5 of the paper, and I would like to congratulate the authors on this success.

If it is not secret know-how, I would like to ask some details about the conditions of the process. It would be especially interesting to know the temperature of the acid before the filtration, the retention time and the temperature of the precipitation. I feel it is easier to proceed on the pilot scale. There will be some complications for the process in a big plant, which are due to the necessity of sufficient cooling systems and retention volume.

The authors have given a very interesting review of the following steps of producing valuable fluorine compounds. Also in these cases the purity of the products is excellent. We hope the authors will succeed in putting into practice the principles they have worked out by applying them in a big way in the industry.

DR. K.V. NAIR (FACT, India): About the two relevant points raised by Dr. Karbe, I would like to give my answers as follows: the know how for precipitation and recovery of fluorine from the processed phosphoric acid as sodium silicofluoride is nothing new. There is, as far as I know, no secret about it. We have done quite a lot of work because nobody else did it in India so far and we had to work out the optimum conditions. That is one of the reasons why we have a very pure material. One of the customers for this product is our neighbour who process the monazite deposit, one of the biggest monazite reserves in the world, managed by the Atomic Energy Commission of the Government of India, which processes this material into thorium and cesium fluorides. Until lately they were recovering these materials as chloride and now they have gone over to the fluoride recovery. Because of this change from rare earth chloride to the rare earth fluoride they just asked us since they have heard that this fertiliser contains a lot of waste fluorine, if it would not be possible for the Research Department to develop a process whereby we could recover this fluorine in a useful form and supply it to them, because during the 6 months when they were asking and before we gave them the product they used to import quite a lot of this fluoride material. First they wanted sodium fluoride, but later they changed their process by making use of sodium silicofluoride itself as the raw material. First when sodium silicofluoride was a raw material for the sodium fluoride process which we had been working, we could afford to get the sodium silicofluoride in a somewhat impure form, because we could solubilize the impurities and make it pure enough for the purpose. But when we started supplying the sodium silicofluoride itself to them they wanted the highest purity possible, and even this we have been able to achieve to their entire satisfaction by changing the process, mainly by filtering the acid, because about 0.1% of suspended impurities in wet process acid was enough to cause sufficient impurity in the product, because 1 t of acid might give 70 kg which would come from 1% of impurities making the impurities higher than 1%. We have not heated the acid at all as it comes from the filter. We are using the acid and I believe the solubility of gypsum in the acid is about 1%. But I think that 1% after the preliminary filtration which is still in solution will take a large number of days to consolidate out, so that in the retention time of 10 to 15 mn we give for this process no gypsum comes out. We have not been able to detect gypsum in the product to any appreciable extent.

MR. MOLLARD (Ugine Kuhlmann, France): I should like to raise several questions concerning the paper in general, and particularly the manufacture of cryolite. Firstly, with regard to the separation of the silica during the ammonia neutralisation, is the filtration on a pilot scale or on an industrial scale with a rotating filter? Secondly, with regard to the speed of decantation indicated by the author for the cryolite, there is an average value of about 0.33 m/hour, corresponding to granules of cryolite of about 1-10 microns. In this case, I do not think that filtration can be very easy. With regard to the density indicated for the cryolite, is it apparent density or real density? During the decomposition of ammoniacal cryolite, corresponding to the manufacture of the aluminium fluoride, NH_4F is released in the calcination furnace. The author states that he uses a tubular furnace of stainless steel. Has he not experienced any corrosion due generally to the formation of bifluoride as a result of the presence of moisture from the filter? Also, I should like to know if the use of aluminium chloride is industrially possible as a means of introducing the aluminium iron in the preparation of cryolite or aluminium fluoride. With regard to the transformation of the ammonia used for the neutralisation of the sodium fluosilicate and its final transformation into ammonium chloride, is it considered economic to recover the ammonia from the ammonium chloride?

DR. NAIR: The first question seems to be about the separation of silica from the reaction mixture by ammoniation of sodium silicofluoride slurry. Actually, we have not done it on a big plant scale. Our capacity in the pilot-plant, which is still operating every day - we only wanted to put this reaction to semi-commercial test - is about 20 kg/hour. We believe it will give much further trouble on scaling up to the maximum of 5 tons or maybe 8 tons capacity in our phosphoric acid plant. We have a 125 t P_2O_5 phosphoric acid plant which can give 9 tons of sodium silicofluoride, so it may 8 or 9 t of cryolite again. So the maximum tonnage at the plant possible with us will be about 8 t and this low capacity pilot-plant was intended to test each process stage regarding the feasibility of operation. For the designed plant which is under construction the filtration is to be done by a rotary waggon filter, whereas in the small scale pilot plant, which is in operation now, we are using a vacuum Nutsche filter. The density is bulk density, and ammonia recovery is at the moment just not done because it is a small plant. But we have found out that at the temperature of the final filtrate in which ammonium chloride is present at about 2%, it is uneconomical to add and recover the ammonia. We have also found that without any trouble, under suction, about 60% of the ammonia could be recovered even without any further external heat, provided we work quickly. The hydration of lime itself is an exothermic process and the temperature goes to about 90, 92, 95° easily and this heat is enough to release easily 50 to 60% of ammonia under vacuum suction. We have not done it on a big scale because, for one thing, considering the price levels of this imported material, even if the whole ammonia is wasted we would still consider the process economic as far as our country is concerned. But the last step I mentioned we are going to investigate further before giving a final answer, because hydration of quick lime can be very exothermic, and we want ammonia.

With regard to the filterability of the cryolite crystals, the product cryolite, even though the calculation has been made from the data presented on the settling characteristics of the final slurry, 1 to 10 microns size, which in its turn gives a rather poor filterability theoretically, neverthe-

less we find that it is one of the most easily filterable crystals. In fact that is the reason, even though it looks a little irrelevant in the paper, why we have given the settling characteristics, because it is really very filterable and washable. And we have also noted that cryolite made by several other methods from ammonium or sodium cryolite gives really bad filterability. Cryolite made by this method, from ammonium cryolite or sodium cryolite by the addition of sodium chloride, give an extremely filterable crystal mass.

MR. MOLLARD: I envy the author for having such an interesting economic situation in India for the recovery of fluorine; this is certainly not the case with us in Europe. With regard to the rate of separation and filtration of the cryolite, I think the separation rate and the dimensions are so low that various processes using fluorine recovered from the phosphate industry offer cryolite of dimensions of 100-300, which can be separated very easily and can even be centrifuged without the use of a filter.

MR. P.R.M. VERSTEEGH (V.K.F. Mekog-Albatros, N.V.): I would like to ask the authors to clarify a few points: on page 4 the authors say that caustic soda is too expensive to use in the precipitation of sodium fluosilicate. In this case, how can trisodium phosphate not be too expensive? I have calculated the amount of fluorine as fluorine precipitated from phosphoric acid from table 2, and I reached the approximate figure of about 60 kg/ton P_2O_5 . On page 4 I note in the use of sodium fluosilicate the approximate figure of 40 kg of fluorine per t P_2O_5 .

On page 4 the authors mention nylon as a filtering material for the phosphoric acid. Could they mention the type of nylon they use there please?

On page 14 in the cryolite a figure for SiO_2 from 0.3 to 0.6% is given. Do the authors think this quality is acceptable for the aluminium industry?

DR. NAIR: Regarding the cost question between trisodium phosphate and caustic soda you will be surprised to learn that in India the company to whom we are selling this product gets trisodium phosphate as a by-product from the monazite phosphate. The monazite is a rare earth phosphate and by decomposition they get all the P_2O_5 as trisodium phosphate, about 20 tons per day, which they sell cheap to us and we give them back our sodium silicofluoride which, according to them, is cheap enough. So it's a two way traffic. So definitively sodium hydroxide, caustic soda, even lye, 40% lye, is costlier for our conditions. This is actually a purely local situation, but we have subsequently tried sodium carbonate also, by dissolving the necessary quantity in the aliquot portion of treated acid from the previous batch and making disodium phosphate. The carbonate makes trisodium at more or less saturated solution, and you pump this in at a metered rate into the filtered phosphoric acid for the precipitation. Again regarding the silica content, we have based our work on the quality specifications of cryolite at the time of writing, which was about 6 months ago. We have based our specifications on the published American specifications where 0.6% was given and we were really happy when we touched 0.3% without any trouble. Subsequently the Indian aluminium industries stipulated that they are not interested in the material if the silica content is more than 0.2%. Now, we have slightly modified the first initial stages of this process so that at the moment we are very easily getting product of 0.1% to 0.125% silica content.

MR. RAEMAKERS (Ugine Kuhlmann, Belgium): With regard to the precipita-

tion of silica from the solution of sodium silicate:

1. How does this precipitation occur? What steps are taken and what is the concentration of the medium? In other words, can you say what is the appearance of the precipitated silica?
2. What type of filter do you use?
3. What is the purity of the calcium silicate obtained with regard to the sodium content?

DR. NAIR: Regarding the removal of silica from the solutions containing ammonium fluoride and sodium fluoride, this is the most secret part of this process. It's a very delicate operation and it requires very strict control to remove the silica so that the product will be within specifications. Ordinarily when we first attempted this we could get only 0.4% silica in the product which we thought would be O.K. for the industry which consumes it. Later when the Indian aluminium industry said they should have a lower specification we thought that it would be very difficult to come to that level. Subsequently, we found that it was really a task which we could luckily overcome by correct conditions of operation just before the filtration of silica. We use an ordinary Nutsche cloth filter for this filtering of the silica. We are able to achieve practically complete removal and the product is very well within the specification requested by the consuming industry.

Regarding the sodium content of the hydrated calcium silicate, this product on the wet filter cake contains about 88 to 92% water. It's a very bad situation, but luckily the precipitate is very washable, so that practically all the sodium could be washed off. On drying we get a reasonably pure product in which sodium is practically absent. This substance is employed for formulating DDT and similar insecticides in our neighbouring concern, and they want a 450% oil absorption, which is measured in terms of water absorption in the laboratory, and our product is anywhere between 600 - 800%. They have never complained about the sodium content although in the initial samples we could detect a little sodium. Later, with 2 or 3 more washings on the filter before drying, the sodium could be almost completely eliminated from the product.