

ISMA* Technical Conference

**Wiesbaden, Germany
11-15 September 1961**

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



THE INTERNATIONAL

SUPERPHOSPHATE

MANUFACTURERS' ASSOCIATION

TECHNICAL COMMITTEE · COMITE DES TECHNICIENS

CONFIDENTIAL

LE/61/61

Received: 3rd July 1961.

TECHNICAL MEETINGS - WIESBADEN

This paper will be presented at the Technical Meetings in Wiesbaden from September 11th to 15th, 1961. It must not be published prior to that date, and in any case, it must not be published without the permission of the author.

THE PILOT PLANT RECOVERY OF CRYOLITE AND ACTIVATED SILICA IN THE MANUFACTURE OF SUPERPHOSPHATE

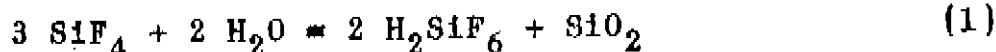
by T.K. Vahervuori,
Rikkihappo Oy,
Finland.

Rikkihappo Oy is the only manufacturer of superphosphate in Finland. The company owns three superphosphate factories with a total annual production capacity of some 400,000 tons super and Kotka phosphate. The manufacture of superphosphate takes place by the Moritz-Standaert method in two factories and by the Rema den process in the third factory.

The phosphate raw material is a mixed powder of which the main part, 70-80 per cent., is Kola apatite and the remainder soft phosphate rock. The mixing of the raw materials takes place in a mill in which the mixture is ground to the desired degree of fineness.

As is well known, a part of the fluorine in raw phosphate rock is first converted in the treatment with sulphuric acid to hydrogen fluoride which, however, immediately reacts with silicates to form silicon tetrafluoride. The acid gases are removed from the den along with the relief gas, which mainly consists of air, but contains also appreciable amounts of moisture and carbon dioxide derived from carbonates and lesser amounts of other gaseous and solid matter in addition to the silicon tetrafluoride and residual hydrogen fluoride.

The silicon tetrafluoride hydrolyses readily in contact with moisture whereupon fluosilicic acid and hydrated silica are formed:



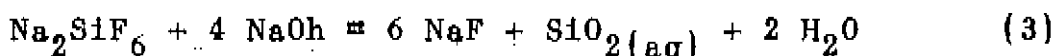
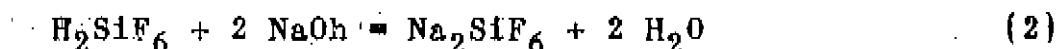
When an attempt is made to collect and utilise the fluorine in phosphate rock, this is primarily a question of collecting

and refining the fluosilicic acid. The finely divided hydrated silica formed in the above reaction occurs as white soot, which name reveals its resemblance to ordinary soot.

On several occasions the recovery of the fluorine compounds in the relief gases from the superphosphate factories has been considered by our company and several series of investigations have been carried out to determine whether this would be an economic proposition.

The first experiments were mainly aimed at producing both soluble and insoluble fluosilicates but the low prices and small demand for such compounds prevented further developments along this line. We therefore began to study the possibilities of producing other fluorine compounds.

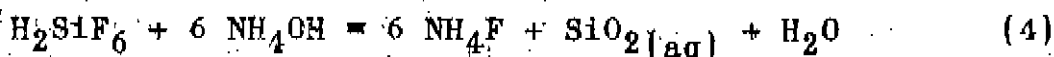
Another method of utilising fluosilicic acid is to decompose it with a base whereupon a fluoride and hydrated silica (SiO_2) are formed. This reaction involves the decomposition of the salt first produced by neutralisation. If soda is used for the base one of the products is sodium fluoride:



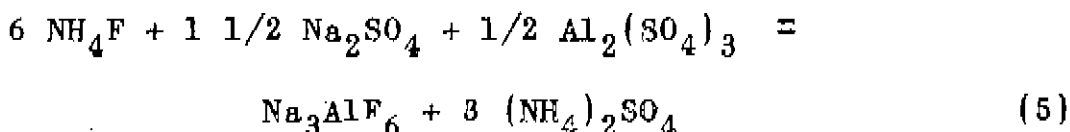
This method of producing fluoride has aroused considerable interest, especially in the USSR. A difficulty associated with this method is the low solubility of sodium fluoride in water (4 parts in 100 parts of water at 15°C). The usual product of the reaction is sodium fluoride, and if some other fluorine compound is desired the fluorine must be first liberated from the salt.

There is no demand for sodium fluoride or fluosilicates in our country and any further synthesis starting from these products would be uneconomical.

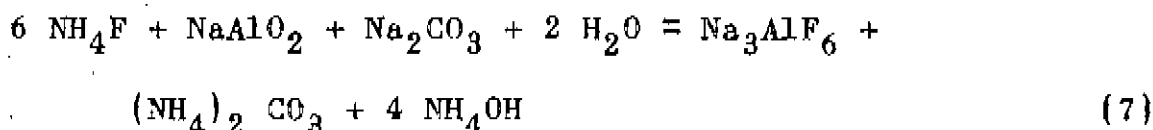
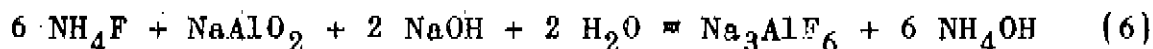
In our studies we finally decided to carry out the neutralization and decomposition of fluosilicic acid with liquid ammonia. The reactions taking place are quite similar to the reactions (2) and (3) mentioned above and can be represented by the over-all reaction equation:



Ammonium fluoride is very soluble in water and hence does not require the use of large volumes of water to leach it from the silica. The salt is, however, difficult to crystallise and has very little if any value as such, but it can be converted into ammonium bifluoride which has a wider use. An important fact is that ammonium bifluoride can be transformed into other compounds by solution reactions. The most important of such compounds commercially is synthetic cryolite, Na_3AlF_6 , which is employed as an opacifier in the glass industry and is used in the manufacture of aluminium metal. The synthesis of cryolite can be effected by different methods depending on whether it is desired to recover the ammonia for re-use or not. If aluminium and sodium sulphates are added to a solution of ammonium fluoride, cryolite and ammonium sulphate are produced:



If the ammonia is to be recirculated, the resulting ammonium sulphate solution must be treated with, for instance, lime. Another method leading to cryolite is to add sodium aluminate and caustic soda or soda ash to the ammonium fluoride solution; ammonia is one of the products:



The process by equation (6) is employed in our pilot plant. One of the advantages of the process is that the main product is low in cost and is widely used, and ammonia, which is a relatively expensive chemical, can be recovered and returned to the process. Another main product of the process is the white soot, activated silica. It is formed both in the hydrolysis of silicon tetrafluoride by equation (1) and in the alkaline decomposition of fluosilicic acid by equation (4).

The first experiments employing the above mentioned process were carried out on the bench scale in a unit made from polythene vessels and drums which had a throughput capacity of 3-4 cubic metres of gas per minute. As the results were promising, it was decided to erect a pilot plant on a scale of 1:10 for the treatment of about 60 cubic metres of gas per minute. One of the first questions that had to be solved in planning the plant was the separation of the fluorine compounds from the relief gases. The hydrated silica produced in reaction (1) has a very large surface area and is highly reactive. Owing to its large surface area, it is able to adsorb considerable amounts of various compounds such as water and, what is important in the present connection, the fluosilicic acid formed in the process. Analyses revealed that the silica produced contained up to 25 per cent of fluosilicic acid and furthermore the greater part, about 75 per cent, of the fluorine in the relief gases was retained. It was quite natural to take advantage of the available first class adsorbent properties. In our pilot plant the relief gas is first passed into a cyclone where the hydrated silica formed in the gas phase and the adsorbed fluosilicic acid are separated from the gas. The material thus separated varies slightly in quantity at different times of the year owing to variations in temperature. When the temperature is high, the dew point of the gas is obviously exceeded and the formation of silica is reduced. After it has passed through the cyclone, the gas is washed with a circulating spray. The solid materials that separate in this stage are collected in a third separator from which the purified gas is vented into the atmosphere. The liquor employed in washing the gas is the ammoniacal filtrate remaining after the isolation of the cryolite.

Two silica slurries are thus obtained in the two stages of purification of the relief gases, one from the cyclone and one from the washing scrubber unit. Both slurries can be combined and treated simultaneously with ammonia. Experience

showed, however, that silicas differing in activity could be obtained by treating the slurries separately. The silica that is formed by reaction (1) in the gas phase is more active than the acid formed by reaction (4) in the liquid phase. The activity was measured as the surface in square metres per gram by the Brunauer method¹⁾ in which the amount of nitrogen taken up by the dried and evacuated sample at the boiling point of liquid oxygen (-182.97° C) is determined. In order to obtain silica of high quality, it is advantageous to separate by leaching and filtration the fluosilicic acid as completely as possible from the hydrated silica coming from the cyclone. The fluosilicic acid remaining after filtration and washing is neutralised, and the silica is then washed, dried and ground. The active surface of the resulting silica is over 100 square metres per gram. Under very favourable conditions materials with active surfaces varying from 180 to 250 square metres per gram have been produced in our pilot plant. The filtrate containing the fluosilicic acid is combined with the liquor from the washing unit and the combined liquor treated separately to prepare fluosilicates. The quality of the silica produced by alkali treatment is better if the silicon content of the liquor is not too high. The solution can be diluted with the filtrate containing ammonium fluoride that is obtained when the silica is separated after the alkali treatment. In this way it is possible to increase the fluorine content of the solution which is used to prepare the cryolite. The activity of the silica precipitated in the alkali treatment has a lower activity, about 70 square metres per gram, than that produced in the gas phase. Both grades of silica are suitable for industrial use. The major consumer of these is the rubber industry and our grades have been found very satisfactory in tests that have been carried out by this industry.

The sodium aluminate used in the preparation of cryolite is produced by heating together caustic soda and alumina hydrate. The cryolite is then prepared in the same or in a separate reaction stage. It separates from the solution as a readily filtered precipitate. Like the silica, the cryolite is dried and ground before being bagged. During the preparation of the cryolite, ammonia escapes from the hot solution as a vapour which may be introduced into the incoming relief gas stream to neutralise the acid gases in the latter. The ammonium fluoride thus formed in the gas phase also has a tendency to form a cloudy precipitate which is as difficult to dissolve as ammonium chloride. It may form a fog at the end of the duct from which relief gas emerges. Another possibility is to wash the ammonia-containing vapour with sulphuric acid and to use the resulting ammonium sulphate solution in the manufacture of mixed fertilisers. The ammoniacal filtrate is used, as already mentioned, as the scrubber liquor.

It may be worth while to discuss certain analytical aspects associated with the process. The prevailing opinion that the analysis of various compounds for fluorine content is one of the most difficult in daily routine work is correct. It could not be expected that the generally employed thorium nitrate titration with its many sources of error, or colorimetric or gravimetric methods could be employed to obtain accurate results within as short a time as is required in factory operations. It was therefore found necessary to develop a rapid and reliable titrimetric method for the analysis of pure ammonium and alkali fluoride solutions. A complexometric method in which the fluoride is first precipitated as calcium fluoride and the excess of calcium added

to the solution is titrated with di-sodium ethylenediaminetetraacetate (e.g. Komplexon III, Titriplex) in the usual manner was tried first. As calcium fluoride is slightly soluble in water, a sharp end point is obtained only when alcoholic solutions are employed. It is furthermore necessary to define the concentrations of alcohol and buffer components and solution volumes accurately.²⁾ The method developed makes it possible for a laboratory technician to report the final result within five minutes after the sample of concentrated fluoride solution has been delivered from the factory to the laboratory.

The experiments that have been carried out so far have been mainly directed at defining appropriate process conditions and reducing losses of chemicals. Less attention has been paid to types and structures of the various component units. The main types of equipment, such as filters and driers, have been clarified and valuable experience in corrosion problems has been collected. The gases and solutions that are handled with the process are highly corrosive. The ducts and cyclones, which were built to our own plans, were first made of 3-mm steel plate and covered with four coats of plastic emulsion paint. It is advisable to use plastic materials and rubber-lined and special steel plates. Whenever plastic emulsion paints are used, particular attention must be paid to the prior preparation of the surfaces and their even coating.

Our pilot plant has to date produced synthetic cryolite and active silica. Our glass manufacturers have made trials with our cryolite and have found the material to fulfill their requirements as to content and amounts of impurities.

The following is a typical analysis:

	F	Al	Na	Fe
Theoretical	54.1	12.9	33.0	-
Found	51.1	14.1	31.1	0.02

The specifications of the glass industry define only the fluorine content (50-52 %) and the maximum iron content (0.1 %).

The activity of the silica is very sensitive not only to the phase in which it is formed but also to the conditions in the various stages of the process. It was already mentioned that the solution to which the alkali is added should have a low silicon content. The temperature must be as low as possible in the neutralisation and the latter must take place rapidly. The equilibria take a long time to proceed to completion owing to the high porosity of the silica. A sufficiently long time must be reserved for the solution to attain the final pH value (9.5 in our process). Attention must also be paid to adequate mixing and effective heat transfer in the designing of the alkali treatment vessels. A factor decisively affecting the quality of the silica is the proper choice of constant operating conditions.

After its precipitation, the silica is filtered, washed, dried and ground to the desired degree of fineness. The washing must be continued until the material is quite neutral. The large surface and slow diffusion of wash liquor through the material make the washing step a slow one. The main objective of the washing is the removal of all the fluorine. This washing must be carried out so thoroughly that only traces

of impurities remain after the fluorine compounds have been removed.

A characteristic aspect of the drying stage is the slow rate of moisture removal which is due to the porosity of the material. The rate of drying can be increased by raising the temperature, but our experience has shown that this affects the activity of the silica unfavorably. Drying in a vacuum at a low temperature has given the best quality silica. Drying with a current of air is effective, but the dustiness of the dried material must then be taken into account.

The pilot plant described can be readily modified, without any major changes in equipment, to permit manufacture of other fluorine compounds. The possibility of preparing fluo-silicates from the fluosilicic acid adsorbed by the hydrated silica formed in the gas phase was already mentioned. The ammonium fluoride formed in the treatment of fluosilicic acid with alkali can be transformed into ammonium bifluoride which finds use in the ceramic, glass and chemical industries. The alkali treatment can be carried out using bases other than ammonia to obtain different fluorides according to demand. As mentioned the manufacture of sodium fluoride by this method has been extensively studied in the USSR.

-
- 1) Stephen Brunauer: "The adsorption of Gases and Vapors", Volume 1 Physical Adsorption, Princeton University Press, 1945, Princeton
 - 2) Seppo Wilska: Suomen Kemistilehti B 31, 400 (1958).

Sulphuric acid
Alumina hydrate
Sodium hydroxide
Sodium (or other) hydroxide
Ammonia

Flow Sheet of Pilot Plant Recovery of Fluorine in the Manufacture of Superphosphate

Waste gas from superphosphate plant

