Pilot Plant Study of an Ammonium Fluoride Process for Recovery of Fluorine from Superphosphate

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About 60% of the fluorine in phosphate rock is evolved when the rock is acidulated with superphosphoric acid to produce high-analysis superphosphate. Pilot plant studies were made of a process for recovering fluorine as ammonium fluosilicate in a Venturi-type scrubber. Substantially all of the fluorine was recovered when the concentration of fluorine in the gases was 0.3 pound per 1000 cubic feet of gas or greater. Loss of ammonia was about 0.04 pound per pound of fluorine recovered. Ammonium fluoride solution was produced by precipitation and separation of silica from the fluosilicate solution. Ammonium fluoride was used to prepare ammonium cryolite for further processing to aluminum fluoride, which has commercial application in the production of aluminum.

DURING TVA's (Tennessee Valley Authority) pilot plant work on production of high-analysis superphosphate from phosphate rock and superphosphoric acid (2), it was found that about 60% of fluorine in phosphate rock was evolved. This compares with the evolution of about 30% of fluorine in phosphate rock when producing normal superphosphate and 10 to 15% when producing triple superphosphate. In considering the construction of a plant for demonstrating the high-analysis superphosphate process, it was important from the standpoint of atmospheric pollution to provide facilities for recovery of fluorine. Because of the relatively high proportion of fluorine recoverable, it appeared that economic credit in the production of high-analysis superphosphate could be realized by recovering fluorine in a marketable form. Also, it was expected that experience gained from a study of the recovery of fluorine from high-analysis superphosphate might be beneficial in other phosphate processes.

As is the case with other superphosphates, most of the fluorine evolved from high-analysis superphosphate is present as silicon tetrafluoride. Only about 6% was found to be in the form of hydrogen fluoride. It has been shown (1, 4) that such gases can be absorbed readily in a slightly acidic solution of ammonium fluoride to form ammonium fluosilicate. The advantages of absorbing silicon tetrafluoride in ammonium fluoride are that precipitation of silica encountered in water scrubbing is avoided, and the scrubbing medium is less corrosive. Silica may be precipitated from ammonium fluosilicate by adding ammonia, and the resultant ammonium fluoride filtrate may be treated further to produce such compounds as calcium fluoride, sodium fluoride, and aluminum fluoride. The present paper describes a pilot plant study of the production of ammonium fluoride

solution from gases evolved during the production of high-analysis superphosphate.

Description of Pilot Plant

High-analysis superphosphate was produced by acidulating Florida phosphate rock (32% P_2O_5) with superphosphoric acid in a pilot plant TVA-type cone mixer. The superphosphate was discharged onto a slat conveyor and then into a stationary box den. The den held about 3 tons of superphosphate and was filled at the rate of 1 ton per hour. The gases from the den were processed in the fluorine recovery pilot plant shown in Figure 1. The gases passed through a 6-inch Venturi-type scrubber, an entrainment separator, and a "demister." The demister consisted of a drum containing a 6-inch layer of coke. From the demister, the gases passed to an exhaust stack. An air jet in the stack was used at times to supplement the draft on the den induced by the scrubber itself.
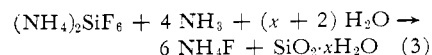
The scrubber sump contained an aqueous solution of ammonium fluosilicate and ammonium fluoride, which was circulated through the scrubber nozzle at the rate of about 28 gallons per minute at a pressure of 60 pounds per square inch. The pH of the scrubber liquor was maintained between 5.5 and 6.0 by the addition of ammonium fluoride–ammonia solution (pH 8.5 to 9.0) recycled to the scrubber from the silica removal step. It was assumed that the ammonium fluoride–ammonia solution reacted with silicon tetrafluoride and hydrogen fluoride according to the following simplified equations.

$$SiF_4 + 2 NH_4F \rightarrow (NH_4)_2SiF_6 \quad (1)$$

and $2 HF + NH_4OH \rightarrow$
$$NH_4HF_2 + H_2O \quad (2)$$
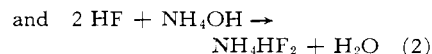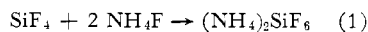
The scrubber sump had a capacity of about 150 gallons. After scrubbing the gases from the den, 100 gallons of the

scrubber liquor were transferred to the filter feed tank. The heel remaining in the sump was sufficient to seal the drain from the entrainment separator and provide liquor at the proper pH for the beginning of a subsequent test. Scrubber liquor was not withdrawn continuously from the sump as might be done in a large plant because it was more convenient to collect it in the sump.

Precipitation of silica was carried out batchwise. Gaseous ammonia was added to the scrubber liquor in the filter feed tank to raise the pH to 8.5 to 9.0.

$$(NH_4)_2SiF_6 + 4 NH_3 + (x + 2) H_2O \rightarrow$$
$$6 NH_4F + SiO_2 \cdot xH_2O \quad (3)$$

$$NH_4HF_2 + NH_3 \rightarrow 2 NH_4F \quad (4)$$

The silica precipitated from solution at this pH was filtered and washed using a rotary vacuum filter 12 inches wide and 18 inches in diameter having an effective filtering area, exclusive of washing area, of 0.92 square foot. The submerged area, the drying and washing area, and the blowing area constituted about 30, 60, and 10%, respectively, of the effective cloth area. The filter normally was operated at a rotational speed of 0.7 r.p.m. The operating vacuum was about 10 p.s.i.g. Heavy wool felt was found to be a satisfactory material for the filter cloth. The filter cake was discarded. About two thirds of the filtrate was recovered as product, and the remainder was returned to the scrubbing system.

Recovery of Fluorine. Typical conditions of operation of the scrubber are shown in Table I. To measure recovery of fluorine from the den gases, samples of gases entering and leaving the scrubber were taken concurrently. The samples were passed through absorbers containing solutions of sodium hydroxide, and the solutions were analyzed for fluorine by the method of Reynolds and Hill (3). Measurements of the recovery of fluorine were made at various periods during the

Table I. Typical Operating Conditions of Fluorine Scrubber

Gas rate, cu. feet/minute (N.T.P.)	217
Inlet gas temperature, °F.	110
Draft at inlet to scrubber, inch H₂O	0.26
Nozzle pressure, lb./sq. inch	60
Scrubber liquor	
Flow rate, gallon/minute	28.2
Temperature, °F.	90
pH	5.6–5.8
F content, grams/liter	
Heel in sump (51 gallons)	63.3
Feed solution (97 gallons)	24.5
Final liquor	64.5

Table II. Effect of Fluorine Concentration in Inlet Gas on Recovery of Fluorine[a]

F in Gas, Lb./Minute, Cu. Feet (N.T.P.)		
Inlet	Exhaust	F Recovered, %
0.032	0.004	88
0.036	0.005	86
0.103	0.011	89
0.229	0.019	92
0.284	0.012	96
0.358	0.012	97
0.447	0.006	99
0.455	0.005	99

[a] Concentration of F in scrubber liquor: 42 to 84 grams/liter. Volume of gas scrubbed: 200 to 250 cu. feet/minute. Volume of scrubber liquor: 28 gallons/minute. Temperature of scrubber liquor: 92° to 104° F.

Figure 1. Fluorine recovery pilot plant

scrubber operation. The concentration of fluorine in the den gases varied widely. Recovery increased from 88 to 99% as the concentration of fluorine in the inlet gas increased from 0.03 to 0.5 pound per 1000 cubic feet of gas (Table II). The concentration of fluorine in the exhaust gas was usually in the range of 0.005 to 0.01 pound per 1000 cubic feet, regardless of inlet gas concentration.

The concentration of fluorine in the scrubber liquor, in the range of 42 to 84 grams per liter, did not affect recovery of fluorine. In some tests the scrubber liquor was heated by means of a steam coil in the sump so that the temperature of the scrubber liquor was as high as 125° F. Increasing the temperature did not appear to have any effect on fluorine recovery.

Loss of Ammonia. Loss of ammonia from scrubber liquor was determined by material balances based on analyses of the heel solution, feed solution, and final scrubber liquor. The average loss of ammonia was about 0.2 pound per hour of operation. The average amount of fluorine recovered per hour was 5.5 pounds, so that loss of ammonia was about 0.04 pound per pound of fluorine recovered.

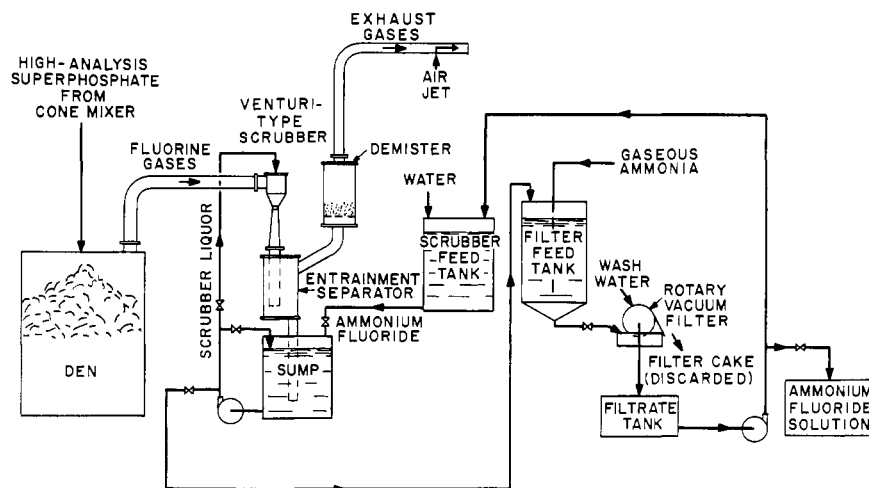Since higher scrubber liquor temperatures may be encountered in large-scale operation than in the pilot plant, some tests were made in which the liquor was heated to temperatures as high as 143° F. The concentration of ammonia in the scrubber liquor was varied from 19 to 58 grams per liter. There was no apparent correlation between the temperature of the liquor or concentration of ammonia and loss of ammonia from the scrubber liquor.

Precipitation and Filtration of Silica. In tests of the precipitation of silica from scrubber liquor (ammonium fluosilicate–ammonium fluoride), ammonia was added to give NH₃:F mole ratios of 0.85 to 1.5. The plot of Figure 2 shows that precipitation of silica increased from 70 to 97% as the NH₃:F mole ratio was increased from 0.85 to 1.1. Further increase in NH₃:F mole ratio to 1.5 did not remove the remainder (2 to 3%) of the silica. The pH's of the ammoniated solutions were in the range of 8.5 to 9.0 as indicated by pH paper. No electrodes suitable for repeated measurements of pH were available. Measurements with pH paper were not precise, so that it was necessary to obtain a reading of at least 8.8 to ensure essentially complete precipitation of silica.

Neither rate of ammoniation (1.1 to 3.7 pound per pound of fluorine per hour) nor temperature of the ammoniated slurry (81° to 142° F.) had a discernible effect on the completeness of the precipitation of silica.

The rate of filtration of silica was affected significantly by the rate of ammoniation and by the temperature of slurry at the time of filtration. When the rate of ammoniation was increased from 1.1 to 3.7 pounds of ammonia per pound of fluorine per hour, and the temperature of the slurry was 104° F., the filtering rate decreased from 77 to 34 gallons per hour per square foot of filter area. Averaged data from a number of tests showed that, when the temperature of the ammoniated slurry was in the range of 80° to 100° F., the filtering rate was about 60 gallons per hour per square foot. When the temperature was in the range of 110° to 130° F., the filter-

ing rate was about 110 gallons per hour. Usually, ammoniation of the scrubber liquor caused an increase in temperature of about 30° F.

The filtering rate also was increased somewhat by allowing ammoniated slurry to age. Normally, filtration of ammoniated liquor was started about 5 minutes after ammoniation. When part of a batch was allowed to age for 3.5 hours before filtering, the filtering rate at the same temperature (128° F.) increased from 78 to 93 gallons per hour per square foot of filtering area.

Limited tests of continuous ammoniation and filtration of the scrubber liquor gave results comparable to those obtained in batchwise tests and indicated that continuous ammoniation would be satisfactory.

About 90% of fluorine in ammoniated slurry was recovered as ammonium fluoride when the filter cake was washed with 1 gallon of water per pound of dry cake. This is equivalent to a rate of 0.28 gallon per gallon of ammoniated slurry when the concentration of fluorine is 60 grams per liter. The cake thickness usually was 1/4 inch, and it contained about 80% of water as determined by vacuum desiccation for 18 hours.

Materials of Construction. Initially, piping made of mild steel was used to recirculate the scrubber liquor (pH 5.5 to 6.0) from the sump to the scrubber nozzle. However, mild steel failed after 50 hours and was replaced with A.I.S.I. type 316 stainless steel. The nozzle was made of A.I.S.I. type 304 stainless steel. The recirculating pump was made of Worthite steel. The entrainment separator, sump, filter feed tank, and filter were of A.I.S.I. type 316 stainless steel. The demister and exhaust ducts were of mild steel. No evidence of serious corrosion was observed in any of this equipment. The Venturi section of the scrubber was cast iron. While corrosion of the Venturi was not obvious, material balances of the scrubber liquor showed that iron from all sources was picked up
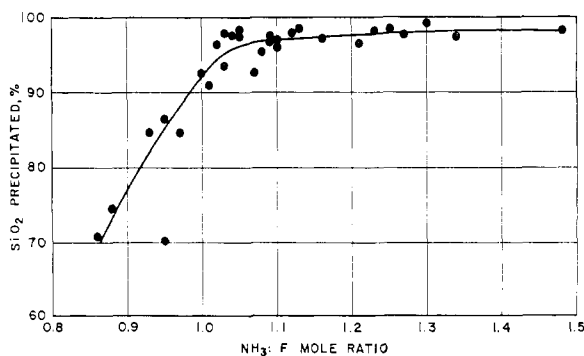
Figure 2. Effect of degree of ammoniation on precipitation of silica

at the rate of about 0.08 pound per hour. It is believed that a large part of this iron came from the Venturi and that cast iron would not be suitable.

Corrosion specimens submerged in the sump for a period of 150 days showed that the attack on A.I.S.I. types 202, 316, 317, and 430 stainless steels and on Ni-o-nel was negligible. The attack on phosphorus bronze D was 4.1 mils per year and the attack on mild steel was 62.1 mils per year.

Preparation of Ammonium Cryolite. Ammonium fluoride typical of that produced in the pilot plant had the following chemical composition:

Amount	F	NH₃	SiO₂	P₂O₅	SO₃	Fe₂O₃
Grams per liter	57.0	62.3	0.55	0.07	7.9	0.06
F:impurity weight ratio	—	—	104	814	7.2	950

Because of the relatively large and growing market for aluminum fluoride for use as a flux in the reduction of alumina, consideration was given to further processing of ammonium fluoride to produce this material or an acceptable substitute. Information from producers of aluminum indicated that the F: impurity weight ratio in fluxing materials should be at least 77 for SiO₂, 460 for P₂O₅, 9.2 for SO₃, and 184 for Fe₂O₃. Tarbutton (4) showed that ammonium cryolite of satisfactory purity could be precipitated from solutions of ammonium fluoride even when the F:P₂O₅ weight ratio was as low as 10. Aluminum fluoride could then be prepared from ammonium cryolite by thermal decomposition or by high-temperature reaction with alumina. Preliminary tests also showed that ammonium cryolite might be used as a substitute for aluminum fluoride in the reduction of alumina. Consequently, quantities of ammonium cryolite were prepared both for use in pilot plant studies of the production of aluminum fluoride and for tests of the suitability of ammonium cryolite as a substitute for aluminum fluoride.

The method, described by Tarbutton, of producing specification-grade ammonium cryolite from ammonium fluoride consisted in adjusting the pH of the ammonium fluoride solution to about 5.5 by addition of sulfuric acid and adding a solution of aluminum sulfate or other soluble aluminum salt to precipitate ammonium cryolite. The reaction is represented by the following equation.

$$12\ NH_4F + Al_2(SO_4)_3 \rightarrow$$
$$2\ (NH_4)_3AlF_6 + 3\ (NH_4)_2SO_4$$
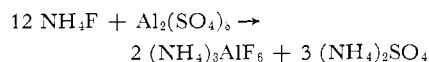
Ammonium cryolite was prepared in the filter feed tank used to precipitate

silica from the scrubber liquor. After adjusting the pH of ammonium fluoride, a solution of aluminum sulfate containing 30 grams of aluminum per liter was added. The solution of aluminum sulfate was prepared in a lead-lined tank either from iron-free aluminum sulfate or by reacting hydrated alumina (Al₂O₃.-3 H₂O) with sulfuric acid. Commercial aluminum sulfate could not be used because of its high iron content. In tests with commercial dry aluminum sulfate containing 0.8% of Fe₂O₃, the amount of iron precipitated with cryolite exceeded the specified limits for iron.

The cryolite slurry was filtered using the same filter and filter cloth as were used in the purification of the scrubber liquor. Filtering rates as high as 300 gallons per hour per square foot were obtained. From 80 to 90% of the fluorine in the purified ammonium fluoride solu-

tion was recovered in the cryolite cake. The filter cake contained 50% water; it dried to a fine, white powder (Table III).

Studies are being made of the further processing of ammonium cryolite to aluminum fluoride by high-temperature reaction with alumina and by thermal decomposition of ammonium cryolite.

Discussion

The feasibility of recovering fluorine from superphosphates by the ammonium fluoride process was demonstrated on a pilot plant scale. Ammonium cryolite sufficiently pure for use in production of aluminum-grade aluminum fluoride was produced. Estimates of the cost of producing other fluorine compounds were not made, but an estimate based on limited data indicated that the production of aluminum fluoride as a by-product from a plant in which about 400 tons per year of fluorine can be recovered would not be profitable. However, larger plants having a greater amount of recoverable fluorine might be able to realize an attractive profit from the production of aluminum fluoride.

An advantage of recovering fluorine as ammonium fluoride instead of fluosilicic acid is that difficulties generally resulting from precipitation of silica are avoided. Another advantage is that the scrubbing medium has a relatively high pH so that corrosion is reduced. It is also believed that whereas two-stage scrubbing usually is required to obtain acid of satisfactorily high concentration, only one stage would be required in the ammonium fluoride process.

Acknowledgment

Literature Cited

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(3) Reynolds, D. S., Hill, W. L., Ind. Eng. Chem., Anal. Ed. 11, 21–7 (1939).
(4) Tarbutton, Grady, Farr, Thad D., Jones, Thomas M., Lewis. Harry T., Jr., Ind. Eng. Chem. 50, 1525–8 (1958).

Table III. Typical Analysis

			Per Cent by Weight			
F	NH₃	Al₂O₃	SiO₂	SO₃	Fe₂O₃	P₂O₅
57.5	23.0	25.5	<0.14	0.5	<0.14	<0.05