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OTS: 60-11,818

JPRS: 2918

5 July 1960

REPORT ON PRODUCTION OF HYDROFLUORIC ACID AND POTASSIUM HYDROFLUORIDE AT WUHAN UNIVERSITY CHEMICAL PLANT

- COMMUNIST CHINA -

TO MAIN FILE

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U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

JPRS: 2918

CSO: 3988-N

I. THE PRODUCTION OF HYDROFLUORIC ACID*

[This is a full translation of an article submitted by the Wuhan University Chemical Plant, appearing in Wuhan Ta-hsueh Tzu-jan K'o-hsueh Hsueh-pao (Wuhan University Journal of Natural Sciences), No 5, 28 January 1959, pages 118-125.]

Hydrofluoric acid is a chemical product of wide application. It is one of the important raw material for new industries and advanced scientific research works. It is used in the atomic energy industry as a indirect raw material for the preparation of U^{235} and as a catalyst in the synthesis of high octane gasoline.

It is an essential raw material in the preparation of inorganic fluorides and organic fluorides. Therefore, the production of hydrofluoric acid should follow the developments of other industries and scientific research works. To meet many demands, we found a small hydrofluoric acid plant with daily production of 25 chin. After six months of operation, production has reached normal level at the present time. Let us introduce the works we are doing in the following:

1. Production method and procedure.

Calcium fluoride and concentrated sulphuric acid are what we use in the preparation of hydrofluoric acid. The principle of chemical reaction is very simple. It is shown in the following formula:

$$CaF_2 + H_2SO_4 \xrightarrow{120 - 130^{\circ}C} CaSO_4 + 2HF \uparrow$$

Why we chose this method? One reason is the easy access of raw material and the other is that the equipment needed is also rather simple.

According to published papers, hydrofluoric acid can be prepared by the reaction of calcium fluoride and ferrous oxide or aluminum oxide with the presents of moisture under high temperature[1], or by the chemical combination of waste fluorine and superheat steam[2]. These methods might have their advantages, but we did not make study in these directions.

Procedure of production:

Place powdered CaF_2 in the reaction crucible and tighten all connecting joints of the apparatus → add concentrated H_2SO_4, 1.35 times the weight of CaF_2, through the opening on the cover (close tight after acid is added) → apply heat, HF is formed → Hydrogen fluoride gas is condensated in condenser at about $0^{\circ}C$ → most part of hydrogen fluoride is condensated to liquid which flows to the first dry receiver. Hydrogen fluoride which still remained in gaseous state will be absorbed by the other receivers containing water → crude product obtained is purified by chemical process → final distillation refining.

Reaction apparatus is shown in the following sketch:

[Footnote to page 1.]

*May we extend our thanks to Peking Chemical Plant (Pei-ching Hua-kung-ch'ang) for their assistance in our preparation and production of hydrofluoric acid.

H_2SO_4 is added through opening here.

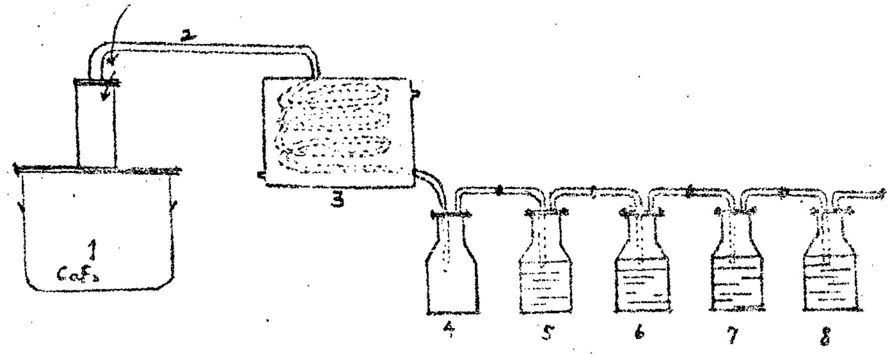

Illustration:

1. Reaction crucible, cast-iron or steel
2. Copper duct
3. Condenser, with spiral copper tubing
4. -8. Receivers, copper

Receiver No. 4 collects about 70 to 80 percent HF (containing H_2SiF_6, 3 - 6%)

The concentration of hydrofluoric acid in receivers 5 to 8 decreases gradually, but the concentration of hydrofluosilicic acid increases.

2. Several problems in the production process.

(1) Gas leaking: Due to low boiling point of hydrogen fluoride ($19.5^{\circ}C$), comparatively high pressure during reaction and strong corrosive property of hydrogen fluoride, gas leaking at the connecting joints of the apparatus is easily to occur, which affects productivity and also is hazardous to the health of the workers. Therefore, gas leaking must be prevented.

Gas leaking occurs at the seam between crucible and its cover, receivers and their covers and also connecting joints of gas ducts. The leak-proof measures taken by us are:

Gaskets that free from the attack of HF is placed between the crucible and its cover (or receivers and their covers) to make it tight. We had used lead gaskets. The thickness of lead gasket that most suitable for such use is about 8 mm without thread. Because lead is a soft metal, too thin tends to change shape and too thick prevents tightening. We also had tried CaF_2 as gasket (CaF_2 is mixed with small amount of water to become gypsum like) which can prevent gas leaking at certain degree but it is inconvenience as compared to lead gasket in using.

Beside the application of lead gasket, the paste of CaF_2 will be applied if the leakage still occurs.

In addition, we used temperature control method to control the speed of reaction and minimize the possibility of leakage. Low fire was maintained in the first four to five hours during the whole process of fourteen to fifteen hours. The temperature was maintained at 120°C at first and then increased gradually until the final one to two hours when the temperature was increased to 300°C in order to accerlerate the evaporation of HF. At the same time, the first receiver was cooled by surrounding ice to prevent the escaping of hydrofluoric acid gas. These procedures have resulted in good product.

(2) The disposal of $CaSO_4$ scale: After the reaction, the residue $CaSO_4$ left in the crucible hardens. If water is used to clean the scale, the iron crucible will be corroded due to the formation of dilute sulphuric acid which attacks the iron. Alkali solution can be used but it is too expensive. The method we used was to let the crucible to cool and then knock off the $CaSO_4$ piece by piece. This procedure is simple and without damaging the crucible.

(3) The refining of crude product: First, the crude products of different concentrations in the receivers are mixed to form about 40 percent concentration HF and then

undergo chemical treatment. The principal impurities in the crude product are:

(a) Volatile impurities, such as: H_2SiF_6 (release SiF_4 by discomposition under heat), HCl, H_2SO_3.

(b) Impurities of low volatility, such as: $SO_4^=$, Pb, Fe, Cu.

To eliminate volatile impurities, $SiF_6^=$ and Cl^-, carbonate salt can be added to form precipitate of insoluble salt which is separated by filtration. As to the $SO_3^=$, oxidizing agent (i.e. $KMnO_4$) is added to form involatile $SO_4^=$ by oxidation. Hydrofluoric acid is finally separated from involatile impurities by distillation.

$BaCO_3$, K_2CO_3 or Na_2CO_3 can be used to eliminate H_2SiF_6. Among them, Barium hydrofluosilicate formed by the addition of $BaCO_3$ has the lowest solubility. Its application has the best effect[3]. But this carbonate salt is expensive and scarce. Therefore, we used Na_2CO_3 instead. The reaction formula is as follows:

$$Na_2CO_3 + H_2SiF_6 = Na_2SiF_6\downarrow + H_2O + CO_2\uparrow$$

This reaction is vigorous. To prevent the loss of HF (heat generated during reaction makes part of liquid to boil and HF gas escapes) and to prevent harm to personnel by the boiling acid, the process should be held under sufficient cooling. At the same time, copper spoon of long arm should be used to add Na_2CO_3 slowly.

The amount of Na_2CO_3 to be added should be adequate to keep down the percentage of H_2SiF_6 in the crude product under 0.25.

4. Distillation: The efficiency of distillation and the quality of distillation product are determined by the length and material of condenser tube. The condensation effect is low if the length of condensation tube is under one meter. If the length is too long it is only a waste of material. According to our experience, 1.5 meters is the best length. Water is generally used for cooling. But during hot weather, ice should be used. We had tried

copper condensation tube which resulted in the presents of copper ion in the product. Silver condenser had been tried and the result was good.

Hydrofluoric acid water solution is a mixture of highest constant boiling point. Different compositions have different boiling points. And the temperature is hard to be controlled during distillation. Therefore, distilled products of different concentrations cannot be obtained. We adopted mixture method to get uniform concentration.

The first 1,000 to 1,500 g distillation product obtained contained more volatile impurities and should be retreated with the crude product.

3. Method of analysis and specifications of product.

The concentration of product and the quantity of hydrofluosilicic acid contained in the product is determined by neutralization method. Other impurities are determined by colorimetric method.[4]

Specifications of our product are as follows:

Hydrofluoric acid 40 percent and above.

Maximum impurities contained:

Distillation residue: 0.01 percent

H_2SiF_6: 0.25 percent

Cl^- : 0.003 percent

SO_2: 0.01 percent

$SO_4^=$: 0.0005 percent

Pb: 0.001 percent

Fe: 0.0003 percent

Our problem during the production was that we spent too much time in preparation before hand and too much time in the disposal of scale. Reaction speed was also too slow. The total time spent was more than twenty-four hours. Therefore, automation will be our objective in the future efforts. And the extension of duration of our apparatus is also an important problem that we shall tackle with.

BIBLIOGRAPHY

1. Strokow F.N. Russ Page 57, 174, May 1948
2. C.R. Schmitt and S.H. Ismiley U.S. 2706, 676
3. A. Ostaszynski & S. Plasek, Bulletin De L'Academie Polonaise Des Science cl. III Vol. V, No. 5,523 1957
4. Rosin: Reagent Chemicals & Standards, Page 211

II. THE PRODUCTION OF POTASSIUM HYDROFLUORIDE

Potassium hydrofluoride is a must in the production of high purity dehydrate hydrofluoric acid and fluorine[1,2,3] and also is an important chemical in the atomic energy and rocketry fields. It is also essential in agriculture, industry and the refining of raw metals.

As early as 1854, E. Fremys, N. Moisgan (and G. Beauega) had done some research in the preparation of potassium hydrofluoride. But their papers revealed that they all used expensive apparatus (platinum crucible and vacuum drying) and produced small amount of the chemical. The demand of potassium hydrofluoride in present day just can not be satisfied by their method. The production must be largely expanded. But mass production carries with it several problems. One is the equipment problem.

Apparantly, platinum apparatus cannot be used in the mass production. The second problem is how to control the chemical process in order to produce specified product. Now, let us introduce our works in these directions in the following:

1. Theory and process.

The reaction formula of potassium carbonate (or KOH) and hydrofluoric acid is:

$$K_2CO_3 + 4HF = 2KHF_2 + CO_2\uparrow + H_2O + \text{heat}$$

or

$$KOH + 2HF = KHF_2 + H_2O + \text{heat}$$

Due to lack of potissium carbonate, we used the second method. Potassium hydroxide is commercially obtainable industrial product. And hydrofluoric acid is obtained from our hydrofluoric acid plant.

Production process:

After completion of reaction between saturated KOH solution and 40% concentration HF * → evaporation, concentration, cooling and crystalization → filtration washing → crystal drying → storage (or packaging) → primary product

Mother liquor → evaporation, concentration, cooling and crystalization → filtration → washing, drying → storage (or packaging) → secondary product.

2. The problem of equipment.

It is quite difficult to equip a plant operated by a university with complete production equipment. Therefore, we added only those apparatus vitally needed and under the condition that the quality of the product would not be affected. We also reconditioned some of our old equipment.

We had silver, copper, plastic and glass apparatus (or porcelain) with paraffin coating which have various degree of anti-corrosive properties toward hydrofluoric acid and fluorides. When heat-resisting is demanded, silver or copper apparatus can be used. And when heat-resisting is not demanded, plastic or glass apparatus are adequate.

3. Several important procedures in the production process.

a. Large amount of heat is generated during the reaction of KOH and HF and the temperature of the solution is gradually raised. Plastic and glass apparatus are not adequate in such circumstance. If silver apparatus is used, the hydrofluoric acid will attack the silver due to extremely high temperature of the solution. This results in the wear of the apparatus and at the same time the appearance of impurity - AgF.

Besides, high temperature of the solution also resulted in the escape of large amount of HF which is hazardous to the health of workers. Toward this problem we took the following measures: cold water bath and controling of introduction speed of chemical. We put the silver

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*Apply filtration if turbidity occurs.

apparatus containing predetermined quantity of hydrofluoric acid in the cold water bath and dropped in saturated KOH solution slowly. Thus, many problems in connection with generating of heat during reaction were prevented.

b. The problem of insuring purity of product: due to impurity of raw material used or other reasons, impurities often appeared in the product. The purification method generally is divided into two directions -- refining of raw material or refining of product. As to the conditions under which refining of raw material or refining of product or both is demanded is determined by the overall consideration.

Impurities of our product were from the following sources:

(1) Industrial pure KOH contains a very small amount of alkali earth metals and heavy metals. The solubility of fluoride of these metals (i.e. CaF_2, MgF_2, FeF_3.....) is low. If they are not eliminated prior to reaction, they are likely to become crystalline at the same time as KHF_2. The separation of these two at this stage is difficult. Therefore, KOH was purified before it was used in our process.*

(2) A part of the silver apparatus (or cooper apparatus) will possibly dissolve in the solution to become AgF (or CuF_2) especially during the concentration when the temperature is high and the corrosive possibility is also high. After our several experiments, we found that AgF (or CuF_2) will not condensate if heating is stopped when a thin layer of crystal appeared on the surface of concentrated solution. The recondensation of mother liquor usually carries AgF or Cuf_2 impurities, which can be separated by recrystallization.

(3) A layer of oxide will form on the surface when copper is heated in the air and the oxide will dissolve in the KHF_2 solution. Therefore, when copper apparatus is used to evaporate potassium hydrofluoride solution, the following procedures should be followed: the copper container should contain about 3/5 volume of solution to be evaporated and the solution should not be increased during the process. This prevents the oxide on the surface of

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*Filtration is the method to eliminate magnesium, calcium and iron impurities.

copper apparatus to dissolve in the solution. According to our experiments, this method is quite effective.

c. Filtration: we tried ordinary glass funnel with paraffin coating in the filtration process but the speed was slow. We later switched to a kind of filter made of copper imitating porcelain filter used in water pump.

d. Drying: KHF_2 will decompose in moisture and release HF. According to published papers, the drying of KHF_2 should be carried out in a vacuum dryer in presents of concentrated sulphuric acid or in 125°-150° C dry air. These methods are not suitable for mass production. After repeated experiments, we put our product in copper evaporator and dry it under heating source (about 150° C) with constant stirring.

The dehydration period of our product when applied in the preparation of fluorine gas and dehydrate hydrofluoric acid, is shorter than commercially obtained KHF_2. The percentage of water contained in the product was determined at 0.2. This is due to absorption of moisture in the air or incomplete dehydration. If the process is carried out in dry air the above phenomenum will be prevented.

4. Procedures of operation:

Predetermined quantity of hydrofluoric acid is placed in silver evaporator under cold water bath and then saturated and purified KOH solution is added drop by drop. When reaction reaches normality (the P^H value is between 6 to 7 when tested by PH test paper) and then stirring in equivalent amount of hydrofluoric acid with plastic rod.

After the reaction is completed, the solution is left to cool. (If precipitate appears the solution is filtered) Then it is poured in cooper evaporator under water bath and heat is applied. When the surface of the solution appears a thin layer of crystal, it is allowed to cool and filtration method is used to separate KHF_2 crystals. They are treated with alcohol once or twice and then dried.

The treatment of mother liquor: repeat the above procedures. If copper evaporator is used and the crystals of KHF_2 obtained from the mother liquor appeared in blue or light blue color (possibly CuF_2) recrystallization method can be applied to refining KHF_2.

The product is sealed in a paraffin coated glass bottle.

5. Analysis and specifications of product:

(1) Fluorine test[6]*: dissolve 0.0002 grams of sample in H_2O inplatinum crucible and control PH value between 2-3 with indicator and then determined by standard $Th(NO_3)_4$ solution.

(2) Determination of maximum impurities: *

a. Chloride: dissolve sample in H_2O, add H_3BO_3, $AgNO_3$, and then take a spectrographic test with blank solution.

b. Heavy metals: dissolve sample in H_3BO_3 solution, add saturated H_2S solution under controlled acidity, and than take a colorimetric test with blank solution.

c. Sulphate salts: eliminate HF by adding acid in the sample, add $BaCl_2$ solution and blank solution for spectrographic test.

d. Iron: dissolve sample in acid solution to eliminate F^-, add ammonium solphate ethyl alcohol solution and KCNS, and then take a colorimetric test with blank solution.

e. Fluosilicate salts: dissolve sample in $AlCl_3$ solution, add HNO_3 and ammonium molybdatesolution, shake well and heat to 50°-60°C, let it cool for five minutes and add HNO_3, dilute the solution and take a colorimetric test with standard solution.

Results of analysis:

KHF_2: (F^-) above 99 %

Chloride (Cl^-): maximum contain less than 0.002%

Sulphate salts ($So_4^{=}$): maximum contain less then 0.02%

Heavy Metal (Pb): maximum contain less than 0.005%

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* For details, see bibliographies 5 and 6.

Iron (Fe): maximum contain less then 0.002%

Fluosilicate salt (K_2SiF_6): maximum contain less than 0.1%

BIBLIOGRAPHY

1. "Industrial Technique in the Manufacture of Fluorine," Chinese Academy of Sciences.

2. "World of Chemistry," 4, 169, (1959), Tseng Fan-chieh.

4. W. Mellor: A Comprehensive Treatise on Inorg and Theoretical Chemistry, Vol II, 516. (1927)

5. Joseph Rosin: Reagent Chem and Standards, 333. (1946)

6. Kolthoff and Steugesr: Volumetric Analysis II, 1320 (1947)

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