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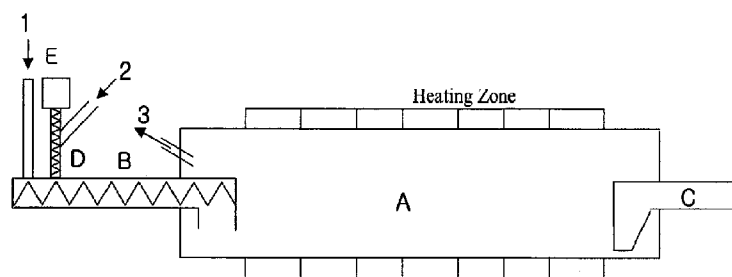
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(54) **Title:** METHOD OF PREPARING ANHYDROUS HYDROGEN FLUORIDE BY USING SODIUM ALUMINUM TETRAFLUORIDE AND REACTION DEVICE FOR THE SAME

[Fig. 1]



(57) **Abstract:** The present invention relates to a method of preparing anhydrous hydrogen fluoride by using sodium aluminum tetrafluoride and a reaction device for the same. More specifically, the present invention relates to a method of preparing anhydrous hydrogen fluoride by mixing and pulverizing sodium aluminum tetrafluoride (NaAlF_4) as a fluoride source with sulfuric acid in a preliminary reactor to obtain gaseous anhydrous hydrogen fluoride (HF) and solid-state material, and treating the obtained solid-state material with heat in a main reactor to obtain gaseous anhydrous hydrogen fluoride and solid sodium aluminum sulfate ($\text{NaAl}(\text{SO}_4)_2$), and a reaction device for the same. According to the present invention, as a fluoride source for preparing anhydrous hydrogen fluoride, an NaAlF_4 byproduct of monosilane production can be reused instead of expensive fluorspar (CaF_2), which is very economical and friendly to the environment. In addition, the production yield of HF can be remarkably improved since a generation of bulky solids is suppressed by uniformly dispersing the viscous reaction intermediate of calcium hydrogen sulfate ($\text{Ca}(\text{HSO}_4)_2$) and the reactants are pulverized finely.

Description

Title of Invention: METHOD OF PREPARING ANHYDROUS HYDROGEN FLUORIDE BY USING SODIUM ALUMINUM TETRAFLUORIDE AND REACTION DEVICE FOR THE SAME

Technical Field

- [1] The present invention relates to a method of preparing anhydrous hydrogen fluoride by using sodium aluminum tetrafluoride and a reaction device for the same. More specifically, the present invention relates to a method of preparing anhydrous hydrogen fluoride by mixing and pulverizing sodium aluminum tetrafluoride (NaAlF_4) as a fluoride source with sulfuric acid in a preliminary reactor to obtain gaseous anhydrous hydrogen fluoride (HF) and solid-state material, and treating the obtained solid-state material with heat in a main reactor to obtain gaseous anhydrous hydrogen fluoride and solid sodium aluminum sulfate ($\text{NaAl}(\text{SO}_4)_2$), and a reaction device for the same. According to the present invention, as a fluoride source for preparing anhydrous hydrogen fluoride, an NaAlF_4 byproduct of monosilane production can be reused instead of expensive fluorspar (CaF_2), which is very economical and friendly to the environment. In addition, the production yield of HF can be remarkably improved since a generation of bulky solids is suppressed by uniformly dispersing the viscous reaction intermediate of calcium hydrogen sulfate ($\text{Ca}(\text{HSO}_4)_2$) and the reactants are pulverized finely. Furthermore, industrial mass production is possible since HF can be produced in a relatively large amount as compared with the weight of the raw materials. And the generated byproduct $\text{NaAl}(\text{SO}_4)_2$ can be reused to obtain sodium sulfate and aluminum sulfate by separation.

Background Art

- [2] Processes of preparing anhydrous hydrogen fluoride by reacting naturally occurring fluorspar with sulfuric acid have been known since the 1940s. In such processes, the production yield of anhydrous hydrogen fluoride has been improved up to now through improvement of reactor materials and forms.
- [3] Calcium hydrogen sulfate ($\text{Ca}(\text{HSO}_4)_2$), which is a reaction intermediate formed during the preparation of anhydrous hydrogen fluoride by using fluorspar and sulfuric acid, is viscous and thus makes starting materials and reaction intermediates agglomerate. Because of the existence of such agglomerated and hard bulky materials, the reactivity is lowered and inward heat transfer during heat treatment becomes difficult, by which the conversion yield to HF is lowered. In addition, such bulky materials adhere to the inner wall of the reactor and block the inside thereof.
- [4] To overcome the above problems, US Patent No. 3,607,121 suggested a rotary kiln

reactor of double-pipe structure. In this rotary kiln reactor of double-pipe structure, raw material agglomeration was reduced by placing a screw for transferring solid materials inside and recycling the reaction byproduct of gypsum (CaSO_4) to the raw fluorspar inlet to dilute fresh fluorspar. However, this device requires a transfer screw therein for reactant recycling and thus the cross-sectional area of the kiln is narrow, which obstructs the movement of reactants and results in accumulation of solids inside the kiln.

[5] US Patent No. 3,718,736 suggested a method for inhibiting agglomeration of reaction intermediates by feeding fluorspar together with the reaction byproduct of gypsum in an amount of molar three times greater than fluorspar in order to dilute raw materials. However, if such gypsum obtained from the finished reaction is fed again, the productivity becomes lower.

[6] US Patent No. 4,120,939 suggested a kind of fluidized bed reactor in which small particles of fluorspar are incorporated into the top of a vertical reactor and dropped down while SO_3 and steam are injected in the bottom to prepare sulfuric acid and gasify it with the heat generated, and the fluorspar falling down from the top is reacted with the gasified sulfuric acid to produce HF. However, this device is complicated and it is hard to optimize the operation conditions, and thus cannot be utilized in mass production.

[7] [PRIOR ART PUBLICATIONS]

[8] <PATENT PUBLICATIONS>

[9] US Patent No. 3,607,121

[10] US Patent No. 3,718,736

[11] US Patent No. 4,120,939

Disclosure of Invention

Technical Problem

[12] To resolve the problems of prior arts as explained above, the present invention has an object of providing an economical and environment-friendly method of preparing anhydrous hydrogen fluoride and a reaction device for the same which can resolve the problem of agglomeration due to the viscous reaction intermediate and improve the production yield remarkably, by which industrial mass production of HF is possible.

Solution to Problem

[13] To achieve the object as explained above, the present invention provides a method of preparing anhydrous hydrogen fluoride comprising the steps of: (1) mixing and pulverizing sodium aluminum tetrafluoride (NaAlF_4) as a fluoride source with sulfuric acid in a preliminary reactor to obtain gaseous anhydrous hydrogen fluoride (HF) and solid-state material, and (2) treating the solid-state material obtained in step (1) with

heat in a main reactor to obtain gaseous anhydrous hydrogen fluoride and solid sodium aluminum sulfate ($\text{NaAl}(\text{SO}_4)_2$).

- [14] Another aspect of the present invention provides a reaction device for preparing anhydrous hydrogen fluoride comprising: (1) a temperature-controllable, kneader-type preliminary reactor having a fluoride source inlet, a sulfuric acid inlet and a mixture outlet; and (2) a temperature-controllable, rotary kiln-type main reactor having a kneader mixture inlet which is connected to the mixture outlet of said kneader-type preliminary reactor, a gaseous anhydrous hydrogen fluoride outlet and a solid product outlet.

Advantageous Effects of Invention

- [15] According to the present invention, as a fluoride source for preparing anhydrous hydrogen fluoride, an NaAlF_4 byproduct of monosilane production can be reused instead of expensive fluorspar (CaF_2), which is very economical and friendly to the environment. In addition, the production yield of HF can be remarkably improved since a generation of bulky solids is suppressed by uniformly dispersing the viscous reaction intermediate of calcium bisulfate ($\text{Ca}(\text{HSO}_4)_2$) and the reactants are pulverized finely. Furthermore, industrial mass production is possible since HF can be produced in a relatively large amount as compared with the weight of the raw materials. And the generated byproduct $\text{NaAl}(\text{SO}_4)_2$ can be reused to obtain sodium sulfate and aluminum sulfate by separation.

Brief Description of Drawings

- [16] Figure 1 schematically represents an embodiment of the reaction device for preparing anhydrous hydrogen fluoride according to the present invention.

Mode for the Invention

- [17] The method of preparing anhydrous hydrogen fluoride and the reaction device for preparing anhydrous hydrogen fluoride according to the present invention are explained in detail below.
- [18] In step (1) of the present method of preparing anhydrous hydrogen fluoride, there is no special limitation to sodium aluminum tetrafluoride (SAF) as a fluoride source. Preferably, an NaAlF_4 byproduct generated in a process of preparing monosilane by reacting SiF_4 gas with a reducing agent of NaAlH_4 , as shown in the following reaction scheme 1) or an NaAlF_4 product prepared by milling a mixture of AlF_3 and NaF mechanically as shown in the following reaction scheme 2) may be used. Particularly, an NaAlF_4 byproduct generated in a process of preparing monosilane is used more preferably in terms of economy and the environment.

[19]

- [20] 1) $\text{SiF}_4 + \text{NaAlH}_4 \rightarrow \text{SiH}_4 + \text{NaAlF}_4$

[21] 2) $\text{AlF}_3 + \text{NaF} \rightarrow \text{NaAlF}_4$

[22]

[23] In step (1) of the present method of preparing anhydrous hydrogen fluoride, sulfuric acid is used in an amount satisfying the following reaction schemes 3) and 4), based on SAF feeding amount.

[24]

[25] 3) $\text{NaAlF}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NaAlF}_2(\text{HSO}_4)_2 + 2\text{HF}$ (main reaction in the preliminary reactor)

[26] 4) $\text{NaAlF}_2(\text{HSO}_4)_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NaAl}(\text{HSO}_4)_4 + 2\text{HF}$ (sub-reaction in the preliminary reactor)

[27]

[28] In step (1) of the present method of preparing anhydrous hydrogen fluoride, SAF may be preferably used in the form of powder (with a size of about 20 μm) or granule (with a size of about 1mm). 98% concentrated sulfuric acid may be used as the sulfuric acid, or oleum may be used to reduce corrosion. There is no limitation to the feeding manner of SAF and sulfuric acid as starting materials. In terms of the process efficiency, continuous feeding is preferable.

[29] As the preliminary reactor used in step (1) of the present method of preparing anhydrous hydrogen fluoride, any reactors capable of mixing and pulverizing SAF and sulfuric acid may be used without a special limitation. However, according to the progress of the reactions of the above schemes 3) and 4) in the preliminary reactor, the amount of sulfuric acid decreases and thus the flowability of the reaction mixture decreases, and a viscous byproduct of $\text{NaAl}(\text{HSO}_4)_4$ is generated. Thus, the preliminary reactor should be able to mix and pulverize the reactants mechanically for uniform mixing. In light of this, a temperature-controllable, kneader-type preliminary reactor is particularly preferred as the preliminary reactor.

[30] There is no particular limitation to the form of kneader. However, it should be able to mix SAF and sulfuric acid uniformly and heat them to 100~300°C so that the reaction may proceed. It should also be able to pulverize the reaction mixture into granules of preferably 1mm size or less and then feed them into the main reactor in the following step. Such a kneader may be manufactured as a double-screw type, or a kneader of general batch type may be used.

[31] In step (1) of the present method of preparing anhydrous hydrogen fluoride, it is preferable to control the reaction conditions so that about 50% of the entire reaction may be conducted, by which gaseous anhydrous hydrogen fluoride (HF) and solid-state material are obtained. Since the preliminary reactor is equipped with a sealing means to prevent the generated gas from being emitted through the inlets of sulfuric acid and SAF, the gaseous anhydrous hydrogen fluoride is transferred to the main reactor and

then discharged outside, and the solid-state material is preferably pulverized to a size of 1mm or less and transferred to the main reactor.

[32] In step (2) of the present method of preparing anhydrous hydrogen fluoride, gaseous anhydrous hydrogen fluoride (HF) and solid sodium aluminum sulfate (SAS) are obtained from the solid-state material obtained in step (1).

[33] HF is obtained according to the above reaction schemes 3) and 4) from unreacted NaAlF_4 and H_2SO_4 existing in the solid-state material obtained in step (1). Gaseous anhydrous hydrogen fluoride and SAS are obtained according to the following reaction scheme 5) from $\text{NaAl}(\text{HSO}_4)_4$ which exists in the solid-state material obtained in step (1) or is generated during the reaction of step (2), and unreacted NaAlF_4 . In addition, gaseous anhydrous hydrogen fluoride and SAS are obtained according to the second reaction of the following reaction scheme 5) from $\text{NaAlF}_2(\text{HSO}_4)_2$ which exists in the solid-state material obtained in step (1) or is generated during the reaction of step (2).

[34]

[35]
$$5) \text{NaAl}(\text{HSO}_4)_4 + \text{NaAlF}_4 \rightarrow 2\text{NaAlF}_2(\text{HSO}_4)_2 \rightarrow 2\text{NaAl}(\text{SO}_4)_2 + 2\text{HF}$$

[36]

[37] For the main reactor used in step (2) of the present method of preparing anhydrous hydrogen fluoride, there is no particular limitation and any reactor may be used as long as it can conduct the reactions of the above schemes 3) to 5) to produce gaseous anhydrous hydrogen fluoride and SAS finally. A temperature-controllable, rotary kiln reactor is preferably used.

[38] According to an embodiment of the present invention, a rotary kiln reactor having a length of 5m, width of 1m, rotation speed of 1~6rpm and inclination of 1/500 can be used. The retention time of the reactant may be adjusted by the feeding amount of raw materials, rotation speed of the kiln or discharging level of the reactant. The reaction temperature is preferably 100~700°C, more preferably 200~500°C and still more preferably 300~500°C. Heating may be performed in an external heating manner. At the end of the rotary reactor, a float may be placed for discharging the reaction product of SAS. It is preferable to control the retention time of the reactant by adjusting the height of the float. The retention time of the reactant is preferably 2 hours to 6 hours. The generated HF passes through a filter to remove fine particles, and is compressed via a compressor and stored in an HF bomb. As for the operation pressure, the reaction is preferably conducted while maintaining a reduced pressure condition of from -20 mmHg to atmospheric pressure in order to facilitate the discharge of the gas generated in the preliminary reactor and main reactor. The solid product of SAS is discharged out of the kiln, and may then be reused by being separated into sodium sulfate and aluminum sulfate.

[39] According to another aspect, the present invention provides a reaction device par-

ticularly suitable for the above method of preparing anhydrous hydrogen fluoride, the device comprising: (1) a temperature-controllable, kneader-type preliminary reactor having a fluoride source inlet, a sulfuric acid inlet and a mixture outlet; and (2) a temperature-controllable, rotary kiln-type main reactor having a kneader mixture inlet which is connected to the mixture outlet of said kneader-type preliminary reactor, a gaseous anhydrous hydrogen fluoride outlet and a solid product outlet. An embodiment of the reaction device of the present invention is schematically represented in Figure 1.

[40] Referring to Figure 1, the present preparation process of anhydrous hydrogen fluoride utilizing the present reaction device is illustrated below.

[41] First, raw materials are fed into kneader (B) as the preliminary reactor through fluoride source inlet (1) and sulfuric acid inlet (2). Sulfuric acid is fed into kneader (B) through reflow-preventing screw (D) connected to motor (E). Kneader (B) is heated to 100~300°C in which the raw materials are preliminarily reacted, mixed and pulverized, and then transferred to kiln (A) as the main reactor. Kiln (A) is heated to 300~500°C and rotated to complete the reaction. The final solid product is discharged out of the kiln through discharge screw (C) and gaseous HF is collected through gas outlet (3).

[42] The present invention is explained in more detail by the following Examples and Comparative Examples. However, the scope of the present invention is not limited by them.

[43]

[44] **[Examples 1~5] Preparation of anhydrous hydrogen fluoride by using kneader and kiln reactors**

[45] The fluoride source used in Examples 1~4 was sodium aluminum tetrafluoride (NaAlF_4) powder (with a size of about 20 μm) or granule (with a diameter of about 1mm) which was a byproduct generated from the reaction of silicon tetrafluoride (SiF_4) and sodium aluminum hydride (NaAlH_4) for preparing monosilane (SiH_4). This fluoride source was dried in a calciner at 300°C and then fed into a kneader reactor with a feeding rate of 6.87kg/hr. The fluoride source used in Example 5 was a product prepared by mechanically milling a mixture of AlF_3 and NaF.

[46] Upon feeding the fluoride source, 98% concentrated sulfuric acid of an equivalent ratio was simultaneously fed into the kneader reactor with a feeding rate of 10.70kg/hr. The reactants were allowed to stay in the kneader reactor for 2 minutes or more. The kneader reactor was maintained at 200°C, and the generated gas was collected through a gas outlet line in the kiln. The reaction intermediates that passed through the kneader were further reacted in the kiln at high temperature to produce anhydrous hydrogen fluoride. The production yield was determined by a titration method, based on the amount of the obtained anhydrous hydrogen fluoride when sulfuric acid was fed for 12 hours. The results are shown in the following Table 1.

[47]

[48] Table 1

[Table 1]

Example	Feeding rate of raw material (kg/hr)		External temperature of kiln (°C)	Yield of anhydrous hydrogen fluoride (%)	Type of SAF
	SAF	Sulfuric acid			
1	6.87	10.70	350 - 400	80	Byproduct after the reaction of NaAlH ₄ and SiF ₄
2	6.87	10.70	400 - 450	86	
3	6.87	10.70	450 - 500	90	
4	3.44	5.35	450 - 500	94	
5	6.87	10.70	350 - 400	94	Mixture of AlF ₃ and NaF

[49]

[50] The yield of anhydrous hydrogen fluoride increased according to the temperature of the kiln. In the case of Example 4 with relatively small amounts of raw materials, the production yield of anhydrous hydrogen fluoride increased by the increase of retention time in the kneader and kiln.

[51]

[52] **[Comparative Examples 1~3] Preparation of anhydrous hydrogen fluoride by using kiln only**

[53] Sodium aluminum tetrafluoride (NaAlF₄) powder (with a size of about 20μm) or granule (with a diameter of about 1mm) was dried in a calciner at 300°C and then fed into a kiln reactor with a feeding rate of 6.87kg/hr. 98% concentrated sulfuric acid of an equivalent ratio was simultaneously fed into the kiln reactor with a feeding rate of 10.70kg/hr to conduct the reaction. The generated gas was collected through a gas outlet line in the kiln. The production yield was determined by the same method as that of the Examples. The results are shown in the following Table 2.

[54]

[55] Table 2

[Table 2]

Comparative Example	Feeding rate of raw material (kg/hr)		External temperature of kiln (°C)	Yield of anhydrous hydrogen fluoride (%)	Type of SAF
	SAF	Sulfuric acid			
1	6.87	10.70	350 - 400	67	Byproduct after the reaction of NaAlH ₄ and SiF ₄
2	6.87	10.70	400 - 450	68	
3	6.87	10.70	450 - 500	72	

[56]

[57] In the cases of reacting SAF and sulfuric acid by using a kiln only without a kneader reactor, the phenomenon of blocking inside the kiln occurred due to the accumulation of reaction intermediates in the kiln reactor.

[58]

[59] **[Comparative Examples 4~5] Preparation of anhydrous hydrogen fluoride by using kneader only**

[60] Sodium aluminum tetrafluoride (NaAlF_4) powder (with a size of about $20\mu\text{m}$) or granule (with a diameter of about 1mm) was dried in a calciner at 300°C and then fed into a kneader reactor with a feeding rate of 6.87kg/hr. 98% concentrated sulfuric acid of an equivalent ratio was simultaneously fed into the kneader reactor with a feeding rate of 10.70kg/hr to conduct the reaction. The diameter of the kneader reactor was 1.2m, and the kneader was embraced with heating jacket to maintain 150°C to 200°C . The generated gas was collected through a gas outlet line connected to a solid storage tank placed at the end of the kneader. The production yield was determined by the same method as that of the Examples. The results are shown in the following Table 3.

[61]

[62] Table 3

[Table 3]

Comparative Example	Feeding rate of raw material (kg/hr)		External temperature of kneader ($^\circ\text{C}$)	Yield of anhydrous hydrogen fluoride (%)	Type of SAF
	SAF	Sulfuric acid			
4	6.87	10.70	150	17	Byproduct after the reaction of NaAlH_4 and SiF_4
5	6.87	10.70	200	32	

[63]

[64] In cases of reacting SAF and sulfuric acid by using a kneader only without a kiln reactor, the solid material was discharged in a wet state, and the yield of anhydrous hydrogen fluoride was low due to the low reaction temperature.

[65]

[66] [EXPLANATION OF THE SYMBOLS]

[67] 1: Fluoride source inlet

[68] 2: Sulfuric acid inlet

[69] 3: Gas outlet

[70] A: Rotary kiln reactor

[71] B: Kneader reactor

- [72] C: Discharge screw
- [73] D: Reflow-preventing screw
- [74] E: Motor

Claims

- [Claim 1] A method of preparing anhydrous hydrogen fluoride comprising the steps of:
- (1) mixing and pulverizing sodium aluminum tetrafluoride as a fluoride source with sulfuric acid in a preliminary reactor to obtain gaseous anhydrous hydrogen fluoride and solid-state material, and
 - (2) treating the solid-state material obtained in step (1) with heat in a main reactor to obtain gaseous anhydrous hydrogen fluoride and solid sodium aluminum sulfate.
- [Claim 2] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein said sodium aluminum tetrafluoride is a byproduct generated in a process of preparing monosilane by reacting SiF_4 gas with a reducing agent of NaAlH_4 , or a product prepared by mechanically milling a mixture of AlF_3 and NaF .
- [Claim 3] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein said preliminary reactor is a kneader reactor.
- [Claim 4] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein the reaction in the preliminary reactor is conducted at 100~300°C.
- [Claim 5] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein said solid-state material obtained in step (1) is pulverized to a size of 1mm or less and transferred to the main reactor.
- [Claim 6] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein said main reactor is a rotary kiln reactor.
- [Claim 7] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein the reaction in the main reactor is conducted at 300~500°C.
- [Claim 8] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein the reaction is conducted while maintaining a reduced pressure condition of from -20mmHg to atmospheric pressure.
- [Claim 9] The method of preparing anhydrous hydrogen fluoride according to claim 1, wherein said solid sodium aluminum sulfate obtained in step (2) is separated into sodium sulfate and aluminum sulfate.
- [Claim 10] A reaction device for preparing anhydrous hydrogen fluoride comprising:
- (1) a temperature-controllable, kneader-type preliminary reactor having a fluoride source inlet, a sulfuric acid inlet and a mixture outlet; and

(2) a temperature-controllable, rotary kiln-type main reactor having a kneader mixture inlet which is connected to the mixture outlet of said kneader-type preliminary reactor, a gaseous anhydrous hydrogen fluoride outlet and a solid product outlet.

[Fig. 1]

