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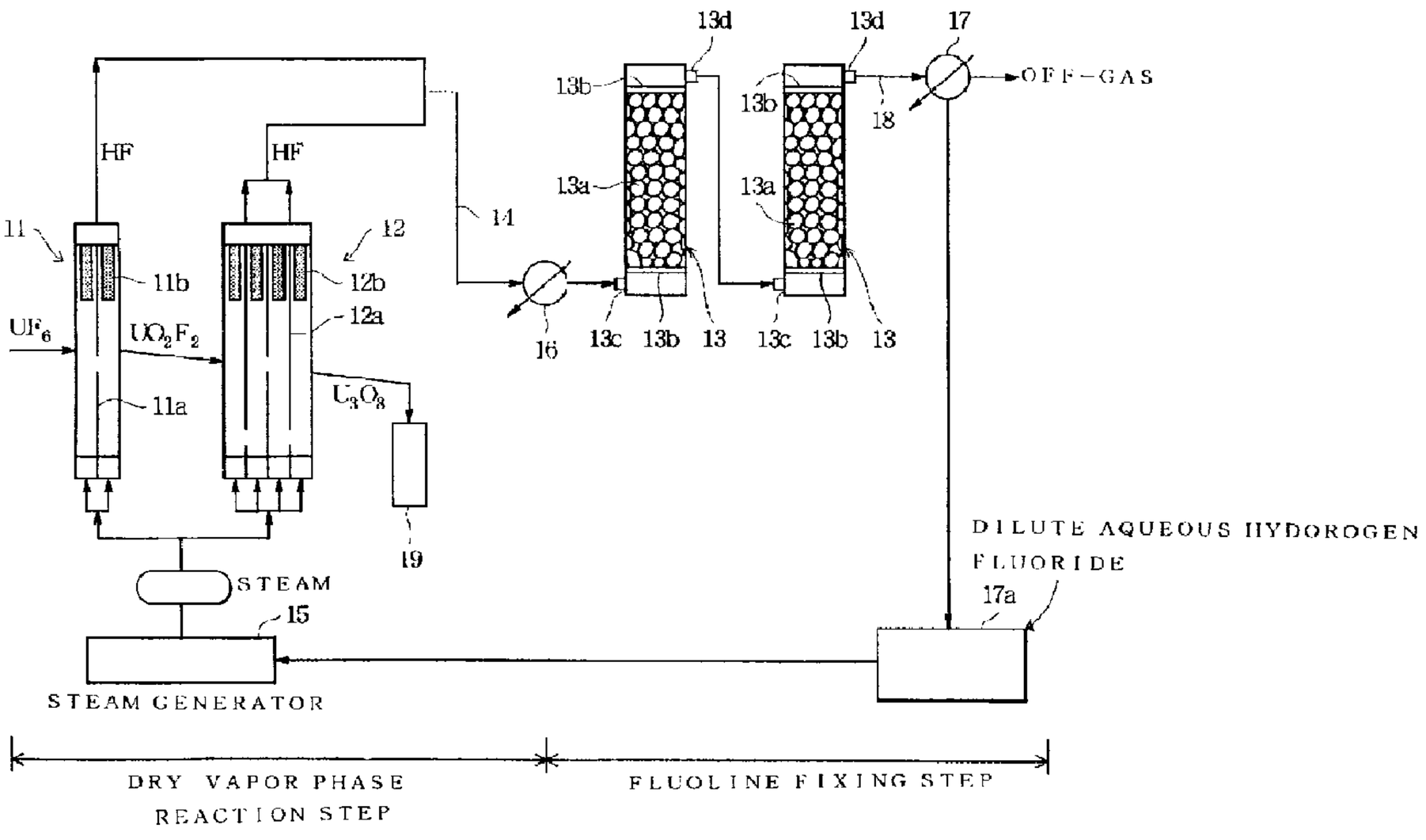
(72) Inventeur/Inventor:
KOIZUMI, HIROMICHI, JP

(73) Propriétaire/Owner:
MITSUBISHI MATERIALS CORPORATION, JP

(74) Agent: RICHES, MCKENZIE & HERBERT LLP

(54) Titre : USINE DE TRAITEMENT DU UF6 APPAUVRI ET METHODE DE TRAITEMENT DU UF6 APPAUVRI
(54) Title: DEPLETED UF6 PROCESSING PLANT AND METHOD FOR PROCESSING DEPLETED UF6



(57) Abrégé/Abstract:
The object of the present invention is to simplify the depleted UF_6 processing plant and processing method and to prevent calcium fluoride to be a fine powder, wherein the processing plant comprises a first fluidized bed reactor for forming UO_2F_2 and hydrogen fluoride by allowing depleted UF_6 to react with steam, a second fluidized bed reactor for forming U_3O_8, hydrogen fluoride and oxygen by allowing UO_2F_2 to react with steam, a gas cooler for cooling hydrogen fluoride at 150 to 300°C, and a fluoride fixing reactor for forming calcium fluoride by allowing cooled hydrogen fluoride to contact calcium carbonate; and wherein the processing process comprises a dry vapor-phase reaction step for forming UO_2F_2 and hydrogen fluoride by allowing depleted UF_6 to react with steam at a temperature of 230 to 280°C, and a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in the dry vapor-phase reaction step to contact granular calcium carbide at a temperature of 150 to 300°C.

ABSTRACT OF THE DISCLOSURE

The object of the present invention is to simplify the depleted UF_6 processing plant and processing method and to prevent calcium fluoride to be a fine powder, wherein the processing plant comprises a first fluidized bed reactor for forming UO_2F_2 and hydrogen fluoride by allowing depleted UF_6 to react with steam, a second fluidized bed reactor for forming U_3O_8, hydrogen fluoride and oxygen by allowing UO_2F_2 to react with steam, a gas cooler for cooling hydrogen fluoride at 150 to 300°C, and a fluoride fixing reactor for forming calcium fluoride by allowing cooled hydrogen fluoride to contact calcium carbonate; and wherein the processing process comprises a dry vapor-phase reaction step for forming UO_2F_2 and hydrogen fluoride by allowing depleted UF_6 to react with steam at a temperature of 230 to 280°C, and a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in the dry vapor-phase reaction step to contact granular calcium carbide at a temperature of 150 to 300°C.

DEPLETED UF_6 PROCESSING PLANT AND METHOD FOR PROCESSING DEPLETED UF_6

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a depleted UF_6 processing plant for processing depleted UF_6 by converting UF_6 into U_3O_8, and a method for processing depleted UF_6.

2. Description of the Related Art

The proportion of depleted UF_6 accumulated in an uranium enrichment plant amount to nearly 90% of the UF_6 starting material, and it is mostly stored by filling in a UF6 cylinder that is a cylindrical sealed storage vessel. However, since this useless substance should be almost permanently stored, there arises a management problem of maintaining the vessel to be free from corrosion over an extended period of time for storage of a large quantity of depleted UF_6, as well as waste of resources and economical deficiencies that a vast amount of fluorine resources are idled in the form of stored UF_6.

A large amount of depleted UF_6 containing a low concentration of U_{235} is accumulated in the enrichment process of U_{235} in the uranium enrichment plant when U_{235} is enriched using UF_6 produced from natural uranium or recovered

UF_6 as a starting material. For solving the problems as hitherto described, the inventors of the present invention have proposed a method for processing depleted UF_6 by converting depleted UF_6 containing a low concentration of U_{235} into U_3O_8 by a dry vapor-phase reaction method (Japanese Unexamined Patent Publication No. 11-79749). The method for processing depleted UF_6 comprises: extracting anhydrous hydrogen fluoride as a by-product with concentrated sulfuric acid and separating anhydrous hydrogen fluoride from dilute sulfuric acid by distillation; further distilling and concentrating dilute sulfuric acid to separate dilute hydrofluoric acid from concentrated sulfuric acid; recycling this concentrated sulfuric acid to the extraction and concentration step while further distilling dilute hydrofluoric acid to separate it into azeotropic hydrofluoric acid and water that contains a small amount of hydrofluoric acid; and mixing azeotropic hydrofluoric acid with dilute hydrofluoric acid in the distillation and concentration step to improve recovery of hydrogen fluoride for recycling it in the nuclear facilities.

However, two distillation columns and one concentration column are required for allowing hydrogen fluoride regenerated in the processing process of depleted UF_6 described above to recycle in the nuclear facilities. For recycling hydrogen fluoride in the existing nuclear

facilities, equipments related to recycling should be additionally installed, causing a problem that supply of anhydrous hydrogen fluoride does not match demands of it. Accordingly, hydrogen fluoride as a by-product generated when depleted UF_6 is converted into U_3O_8 is also desired to be recovered and stored so that it can be readily recycled.

The method for recovering and storing fluorine known in the art include forming calcium fluoride by a fixing reaction of fluorine to calcium, followed by storage of calcium fluoride. The inventors of the present invention have proposed a method for recovering granular calcium fluoride by allowing a solution mainly containing hydrogen fluoride to contact granular calcium carbonate, and an equipment to be used for the method (Japanese Unexamined Patent Publication No. 10-330113). This equipment comprises a storage tank for storing a solution containing 10 to 60% of hydrogen fluoride, a first cooler for cooling the solution stored in the storage tank to 0 to 5°C, a reaction tank for forming a solution containing granular calcium fluoride by adding granular calcium carbonate to the solution at a temperature of 0 to 5°C that is fed from the storage tank, and a solid/liquid separator for separating granular calcium fluoride from the solution containing it. This method is so devised that fluorine can be recovered with a high yield by forming calcium fluoride by cooling the

reaction solution to 0 to 5°C in the first cooler.

However, the hydrogen fluoride gas as a by-product generated when UF_6 is converted into U_3O_8 should be once turned into an aqueous hydrogen fluoride solution containing 10 to 60% of hydrogen fluoride, in order to recover hydrogen fluoride as a by-product which is generated when depleted UF_6 is converted into U_3O_8 using the equipment disclosed in Japanese Unexamined Patent Publication No. 10-330113, causing a problem that facilities related to the foregoing conversion process should be additionally installed. It is also a problem in the conventional process described above that the recovery work becomes so complicated if hydrogen fluoride as a by-product generated in converting UF_6 into U_3O_8 could not be recovered. Also, there is a drawback that calcium fluoride formed by recovery of hydrogen fluoride tend to be a fine powder.

SUMMARY OF THE INVENTION

Accordingly, the object of the present invention is to provide a depleted UF_6 processing plant that is able to simplify the facilities and processes while enabling to prevent recovered calcium fluoride to be a fine powder, and a method for processing depleted UF_6.

In one aspect, the present invention provides a method for improving the depleted UF_6 processing plant as shown in

FIG. 1, comprising a first fluidized bed reactor 11 constructed so that UO_2F_2 and hydrogen fluoride can be formed by allowing depleted UF_6 to react with steam, and a second fluidized bed reactor 12 constructed so that U_3O_8, hydrogen fluoride and oxygen can be formed by allowing UO_2F_2 to further react with steam.

Features of the construction comprises a gas cooler 16 for cooling hydrogen fluoride generated in the first and second fluidized bed reactors 11 and 12 to 150 to 300°C, and a fluorine fixing reactor 13, which is filled with granular calcium carbonate 13a so that hydrogen fluoride cooled to 150 to 300°C with the gas cooler 16 can pass through, capable of forming granular calcium fluoride by allowing hydrogen fluoride passing through the reactor to contact granular calcium carbonate 13a.

In the plant as described above, gaseous hydrogen fluoride generated in the first and second fluidized bed reactors 11 and 12 is directly introduced into the fluorine fixing reactor 13. UF_6 is converted into U_3O_8 simultaneously with forming granular calcium fluoride by allowing hydrogen fluoride to contact calcium carbonate 13a in the fluorine fixing reactor 13, thereby recovering hydrogen fluoride as a by-product.

Calcium carbonate 13a filled in the fluorine fixing reactor 13 preferably has a grain size of 350 to 800 µm.

When the grain size is less than 350 μm, hydrogen fluoride flow is inhibited while, when the grain size exceeds 800 μm, the total surface area of calcium carbonate **13a** diminishes to reduced the amount of calcium fluoride formed.

It is preferable that a plurality of cylinders in which calcium carbonate **13a** is housed are arranged, for example, on a circle so as to be exchangeable one another in the fluorine fixing reactor **13**. After converting calcium carbonate **13a** into calcium fluoride by allowing hydrogen fluoride to pass through one or two of the plural cylinders, the cylinders in which calcium carbonate has been converted into calcium fluoride are replaced with another fresh cylinders to enable additional hydrogen fluoride to pass through the cylinders. A continuous processing of depleted UF_6 is thus made possible when a fluorine fixing reactor capable of readily exchanging calcium carbonate is used.

The method for processing depleted UF_6 preferably comprising: a dry vapor-phase reaction step for forming UO_2F_2 by allowing depleted UF_6 to react with steam at 230 to 280°C, followed by forming U_3O_8, hydrogen fluoride and oxygen by allowing UO_2F_2 to further react with steam at 600 to 700°C; and a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in the dry vapor-phase reaction step to contact granular calcium carbonate at 150 to 300°C.

In the method described above, UO_2F_2 grains with a mean grain size of 100 to 250 μm and a bulk density of 3.5 g/cm^2 or more, and hydrogen fluoride are formed by allowing depleted UF_6 to react with steam by adjusting the reaction temperature at 230 to 280°C; and U_3O_8, hydrogen fluoride and oxygen are formed by further allowing the UO_2F_2 grains having the properties as described above to react with steam by adjusting the reaction temperature at 600°C or more. U_3O_8 thus formed has an approximately uniform mean grain size and an increased bulk density by about 10%, besides having good fluidity and being easy in handling to improve storage efficiency.

Grains of calcium fluoride can be prevented from being collapsed to maintain granular shape of calcium fluoride by allowing gaseous hydrogen fluoride to directly contact granular calcium carbonate **13a** by maintaining the temperature above the boiling point, or at 150 to 300°C, of hydrogen fluoride formed in the dry vapor-phase reaction step, thus making handling of calcium fluoride formed by the fluoride fixing reaction easy.

In accordance with an another aspect of the present invention, the dilute hydrofluoric acid formed in the fluorine fixing step described above is used for the steam to be used in the dry vapor-phase reaction process.

In the method as described above, efflux of the

secondary waste water is reduced by using the dilute hydrofluoric acid solution discharged in the fluorine fixing reaction step as steam for the dry vapor-phase reaction step.

In another aspect, the present invention provides a depleted UF_6 processing plant comprising: a first fluidized bed reactor having at least one plate and configured to react depleted UF_6 with steam at a temperature of 230 to 280° C. and produce UO_2F_2 and hydrogen fluoride, the at least one plate forming a plurality of communicated chambers in the first fluidized bed reactor; a second fluidized bed reactor having at least one plate, connected to the first fluidized bed reactor and configured to react the UO_2F_2 with steam at a temperature of 600 to 700° C. and produce U_3O_8, hydrogen fluoride and oxygen, the at least one plate forming a plurality of communicated chambers in the second fluidized bed reactor; and a fluorine fixing reactor including granular calcium carbonate and connected to the first and second fluidized bed reactors, the fluorine fixing reactor being configured to react the hydrogen fluoride generated in the first and second fluidized bed reactors with the granular calcium carbonate at a temperature of 150 to 300° C. and produce granular calcium fluoride.

In another aspect, the present invention provides a method for processing depleted UF_6 comprising the steps of: reacting the depleted UF_6 and steam at a temperature of 230 to 280° C. in a first fluidized bed reactor having at least one plate and configured to react depleted UF_6 with steam to produce UO_2F_2 and hydrogen

fluoride, the at least one plate forming a plurality of communicated chambers in the first fluidized bed reactor; reacting the UO_2F_2 with steam at a temperature of 600 to 700°C in a second fluidized bed reactor having at least one plate and configured to react UO_2F_2 with steam to produce U_3O_8, hydrogen fluoride and oxygen, the at least one plate forming a plurality of communicated chambers in the second fluidized bed reactor; and reacting the hydrogen fluoride generated in the first and second fluidized bed reactors with granular calcium carbonate in a fluorine fixing reactor at a temperature of 150 to 300°C to produce calcium fluoride.

In another aspect, the present invention provides a depleted UF_6 processing plant comprising a first fluidized bed reactor constructed so that UO_2F_2 and hydrogen fluoride can be formed by allowing depleted UF_6 to react with steam and a second fluidized bed reactor constructed so that U_3O_8, hydrogen fluoride and oxygen can be formed by allowing UO_2F_2 to further react with steam, provided with:

a gas cooler for cooling hydrogen fluoride generated in said first and second fluidized bed reactors to 150 to 300°C; and

a fluorine fixing reactor, filled with granular calcium carbonate so that hydrogen fluoride cooled to 150 to 300°C with the gas cooler can pass through, capable of forming granular calcium fluoride by allowing hydrogen fluoride passing through the reactor to make contact with granular calcium carbonate.

In another aspect, the present invention provides a depleted UF_6 processing plant comprising first and second fluidized bed reactors, wherein said fluidized bed reactors are plate type fluidized bed reactors having a plurality of chambers, wherein said processing plant is adapted to carry out the following method steps:

a dry vapor-phase reaction step for forming U_3O_8, hydrogen fluoride and oxygen at reaction temperatures of the first fluidized bed reactor and second fluidized bed reactor of 230 to 280°C and 600 to 700°C, respectively; and

a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in said dry vapor-phase reaction step to react with granular calcium carbonate at a temperature of 150 to 300°C.

In another aspect, the present invention provides a depleted UF_6 processing plant adapted to carry out the following method steps:

a hydrofluoric acid recovery process consists of three steps which is formed in the dry vapor phase reaction according to any one of claims 1 and 2,

wherein the first step is extraction and distillation for separating anhydrous hydrogen fluoride from dilute hydrofluoric acid by extraction using concentrated sulfuric acid,

wherein the second step is concentration of diluted sulfuric acid, which is formed in above mentioned extraction and distillation step, by evaporation of diluted hydrofluoric acid and concentrated sulfuric acid is refused in the first step, and

wherein the third step is refining distillation of diluted hydrofluoric acid, which is formed in the second step, to separate to azeotropic hydrofluoric acid is feed to the first step; and a fluorine fixing step for water containing a trace amount of hydrofluoric acid, which formed in third step, to form granular calcium fluoride by reacting with granular calcium carbonate.

In another aspect, the present invention provides a method for processing depleted UF_6 comprising:

three steps for hydrofluoric acid recovery which is formed in the dry vapor phase reaction according to any one of claims 1 and 2,

wherein the first step is extraction and distillation for separating anhydrous hydrogen fluoride from dilute hydrofluoric acid by extraction using concentrated sulfuric acid,

wherein the second step is concentration of diluted sulfuric acid, which is formed in above mentioned extraction and distillation step, by evaporation of diluted hydrofluoric acid and concentrated sulfuric acid is refused in the first step, and

wherein the third step is refining distillation of diluted hydrofluoric acid, which is formed in the second step, to separate to azeotropic hydrofluoric acid is feed to the first step; and a fluorine fixing step for water containing a trace amount of hydrofluoric acid, which formed in third step, to form granular calcium fluoride by reacting with granular calcium carbonate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a system flow diagram of the processing method and processing plant according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will now be described in detail with reference to the drawing of the embodiment according to the present invention.

As shown in FIG. 1, the depleted UF_6 processing plant according to the present invention comprises: a first fluidized bed reactor 11 for forming UO_2F_2 and hydrogen fluoride by allowing depleted UF_6 to react with steam; a

area of the plant is suppressed by using the plate type fluidized bed reactors. The plate type fluidized bed reactors in this embodiment comprises plural chambers divided by one or plural partition plates **11a** and **12a** vertically disposed in the fluidized bed. Gas/solid separation filters **11b**, **12b** are provided at the upper parts of the plural chambers divided by the partition plates **11a** and **12a**. Heaters (not shown) are provided in the first and second fluidized bed reactors **11** and **12**, each heater being so constructed as to enable the reaction temperature in respective fluidized bed reactors **11** and **12** to be controlled. Steam introduced into the first and second fluidized bed reactors **11** and **12** from their bottoms is generated in a steam generator **15**.

The fluorine fixing reactor **13** comprises plural slender cylinders filled with granular calcium carbonate **13a**. A gas inlet port **13c** is provided at the bottom of each cylinder, and a discharge port **13d** is provided at the top of the cylinder for discharging the gas passing through filled calcium carbonate **13a**. A pair of partition plates **13b** and **13b**, on which a number of holes through which the discharge gas can pass through but granular calcium carbonate **13a** cannot are provided, are provided at the top and bottom in the cylinder, and calcium carbonate **13a** is filled between this pair of the partition plates **13b** and **13b**. A plurality

of cylinders (not shown) are disposed on a circle to be exchangeable one another, and hydrogen fluoride is made to contact calcium carbonate **13a** filled in two cylinders among the plural cylinders. Actually, the inlet **13c** of the first cylinder is connected to the first and second fluidized bed reactors **11** and **12** via a first piping **14**, and a gas cooler **16** is provided at the first piping. The discharge port **13d** of the first cylinder is connected to the inlet port **13c** of the second cylinder, and the discharge port **13d** of the second cylinder is connected to a condenser **17** via a second piping **18**. The fluorine fixing reactor **13** is so constructed as to be able to form granular calcium carbonate by allowing gaseous hydrogen fluoride generated in the first and second fluidized bed reactors **11** and **12** to sequentially contact granular calcium carbonate **13a** filled in the first and second cylinders. The cylinders are arranged so that additional hydrogen fluoride can be fed by replacing the saturated cylinders with fresh cylinders.

The method for processing depleted UF_6 according to the present invention using the plant having the construction as described above will be described below.

<u>Dry vapor-phase reaction step</u>

The reaction temperature in the first fluidized bed reactor **11** for allowing depleted UF_6 to react with steam is controlled to 230 to 280°C with a heater (not shown), while

the reaction temperature in the second fluidized bed reactor 12 for allowing UO_2F_2 to further react with steam is controlled to 600 to 700°C. UO_2F_2 granules with a mean grain size of 100 to 250 μm and a bulk density of 3.5 g/cm^3, and hydrogen fluoride are formed by allowing depleted UF_6 to react with steam in the first fluidized bed reactor 11 controlled to 230 to 280°C. When the reaction temperature in the first fluidized bed reactor 11 is less than 230°C, physical properties of the powder may be deteriorated, while the reaction temperature exceeding 280°C is not desirable since the bulk density is a little decreased. Accordingly, the preferable reaction temperature in the first fluidized bed reactor 11 is 180 to 260°C.

U_3O_8, hydrogen fluoride and oxygen are formed by allowing the UO_2F_2 granules having the properties as described above to further react with steam in the second fluidized bed reactor 12 controlled to 600 to 700°C. The recovered U_3O_8 powder is accommodated in a storage vessel 19 for storage of an extended period of time. U_3O_8 granules having a mean grain size of 100 to 250 μm, which endows the granules good fluidity and easy handling, and a bulk density of 3.5 g/cm$_3$, which improves storage efficiency, can be obtained by processing UF_6 as described above. A reaction temperature of the second fluidized bed reactor 11 of less than 600°C is not desirable since the reaction ratio may

decrease while the equipments may be corroded at a temperature over 700°C. Accordingly, the particularly preferable temperature is from 600 through 650°C.

Fluorine fixing process

Hydrogen fluoride as by-products of the first fluidized bed reactor **11** and second fluidized bed reactor **12** is introduced into the fluorine fixing reactor **13** via the first piping **14**. The temperature of hydrogen fluoride passing through the first piping is controlled to 150 to 300°C with the gas cooler **16**. Hydrogen fluoride controlled to 150 to 300°C flows from the gas inlet **13c** of the first and second cylinders into the bottom partition plate **13b** and advances through calcium carbonate granules. Calcium fluoride is formed by allowing hydrogen fluoride to react with calcium carbonate **13a** among the calcium carbonate granules **13a**, thereby trapping hydrogen fluoride. A part of hydrogen fluoride may be condensed when the reaction temperature is less than 150°C, while a temperature of over 300°C is not desirable since grain size of resultant calcium fluoride becomes too fine. Accordingly, the preferable reaction temperature for hydrogen fluoride is from 200 through 250°C.

The gas after trapping hydrogen fluoride is discharged from the discharge port **13d** by passing through the upper partition plates **13b** in the second cylinder.

The gas discharged from the discharge port **13d** is

transferred to the condenser **17** through the second piping **18**. The dilute aqueous hydrogen fluoride solution liquefied and recovered with the condenser **17** is temporarily received in the storage vessel **17a** for utilizing it thereafter. Since the content of fluorine fractions in the aqueous hydrogen fluoride solution received in the storage vessel **17a** is so small that corrosion of the stem generator **15** is negligible besides little influencing on the reaction characteristics in the first and second fluidized bed reactors **11** and **12**. Therefore, the aqueous hydrogen fluoride solution can be used for generating steam for the dry vapor-phase reaction process after being transferred to the steam generator **15**.

Examples

Example 1

Hydrogen fluoride was processed in the fluorine fixing reactor **13**. Actually, 10 kg each of calcium carbonate granules **13a** with a grain size of 350 μm were filled into the first and second cylinders. After adjusting the temperature of hydrogen fluoride at 200°C with the gas cooler, fluorine was fixed by feeding the gas at a feed rate of 2000 litters/hour. The hydrogen fluoride gas discharged from the second cylinder was recovered with the condenser **17** to obtain a recovery rate of 2.5 litters/hour of the dilute aqueous hydrogen fluoride solution, and the concentration of fluorine in the solution was measured to be 800 ppm. Feed

of hydrogen fluoride was stopped 30 minutes after, and calcium fluoride formed by conversion of calcium carbonate was recovered.

Comparative Example 1

Hydrogen fluoride was processed by the equipment disclosed in Japanese Unexamined Patent Publication No. 10-330113 that has been described in the related art. Actually, 1.3 kg of calcium carbonate granules were added to 1 litter of an aqueous solution containing 50% of hydrogen fluoride while adjusting the temperature at 30°C. After a solution containing calcium fluoride granules had been formed, calcium fluoride was recovered by solid/liquid separation.

Evaluation

Purity of recovered calcium fluoride, conversion ratios and purity of hydrogen fluoride, concentrations of aqueous hydrogen fluoride solution condensed in the condenser, and purity of calcium fluoride granules were determined with respect to Example 1 and Comparative Example 1. The results are shown in TABLE 1.

TABLE 1

	EXAMPLE 1	COMPARATIVE EXAMPLE 1
PURITY OF CALCIUM FLUORIDE	97% OR MORE	97% OR MORE
CONVERSION RATIO OF FLUORINE	99% OR MORE	90% OR MORE

CONCENTRATION OF AQUEOUS HYDROGEN FLUORIDE AFTER THE REACTION	800 PPM	5% BY WEIGHT
PROPORTION OF CALCIUM FLUORIDE GRANULES HAVING A PARTICLE SIZE OF 100 μm OR LESS	LESS THAN 5%	LESS THAN 15%

Table 1 clearly shows that, although relatively high purity calcium fluoride is obtained in both Example 1 and Comparative Example 1, fluorine is converted into calcium fluoride with a higher conversion ratio in Example 1 than in Comparative Example 1, because hydrogen fluoride is directly introduced into the fluorine fixing reactor in a gaseous state.

Since the concentration of aqueous hydrogen fluoride solution in Example 1 after the reaction is 800 ppm, corrosion of the steam generator is negligible even when the dilute aqueous hydrogen fluoride solution is used as a steam source in the dry vapor-phase reaction process, leaving no influence on the reaction characteristics of the first and second fluidized bed reactors 11 and 12.

Moreover, while the proportion of the calcium fluoride particles having a grain size of 100 μm or less formed after forming the fine powders was less than 15% in Comparative example 1, the corresponding proportion in Example 1 was less than 5%. Therefore, formation of a fine powder is more suppressed in Example 1 than in Comparative Example 1.

The present invention provides a fluorine fixing reactor that is able to form granular calcium fluoride by allowing hydrogen fluoride cooled with a gas cooler to make contact with granular calcium carbide, thereby enabling granular calcium fluoride to be formed by allowing gaseous hydrogen fluoride to contact calcium carbonate after directly introducing gaseous hydrogen fluoride into the fluorine fixing reactor. Therefore, needs of equipments that have been required in the conventional process such as a distillation column and concentration column, or a converter for converting gaseous hydrogen fluoride into an aqueous solution of hydrogen fluoride and a storage tank for storing the solution, can be eliminated, making it possible to simplify the depleted UF_6 processing plant.

The present invention also provides a gas cooler for cooling hydrogen fluoride generated in the first and second fluidized bed reactors at a temperature of 150 to 300°C, thus enabling hydrogen fluoride generated in the first and second fluidized bed reactors to be directly introduced into the fluorine fixing reactor. Accordingly, the depleted UF_6 processing process can be simplified besides enabling collapse of calcium fluoride particles to be prevented by allowing hydrogen fluoride to contact calcium carbonate at a temperature of 150 to 300°C. Consequently, granular shapes of calcium fluoride is maintained to make handling of

calcium fluoride for fixing fluorine easy in the following processing steps.

Efflux of the secondary waste water can be reduced by using the dilute aqueous hydrogen fluoride solution generated in the fluorine fixing step for steam in the dry vapor-phase reaction step, thereby reducing the processing plant size to enable depleted UF_6 to be cheaply processed.

CLAIMS

1. A depleted UF_6 processing plant comprising a first fluidized bed reactor constructed so that UO_2F_2 and hydrogen fluoride can be formed by allowing depleted UF_6 to react with steam and a second fluidized bed reactor constructed so that U_3O_8, hydrogen fluoride and oxygen can be formed by allowing UO_2F_2 to further react with steam, provided with:

a gas cooler for cooling hydrogen fluoride generated in said first and second fluidized bed reactors to 150 to 300°C; and

a fluorine fixing reactor, filled with granular calcium carbonate so that hydrogen fluoride cooled to 150 to 300°C with the gas cooler can pass through, capable of forming granular calcium fluoride by allowing hydrogen fluoride passing through the reactor to make contact with granular calcium carbonate.

2. A depleted UF_6 processing plant comprising first and second fluidized bed reactors, wherein said fluidized bed reactors are plate type fluidized bed reactors having a plurality of chambers, wherein said processing plant is adapted to carry out the following method steps:

a dry vapor-phase reaction step for forming U_3O_8, hydrogen fluoride and oxygen at reaction temperatures of the first fluidized bed reactor and second fluidized bed reactor of 230 to 280°C and 600 to 700°C, respectively; and

a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in said dry vapor-phase reaction step to react with granular calcium carbonate at a temperature of 150 to 300°C.

3. A depleted UF_6 processing plant according to Claim 2, wherein a dilute aqueous hydrogen fluoride solution formed in the fluorine fixing step is used for the steam to be used in the dry vapor-phase reaction step.

4. A depleted UF_6 processing plant adapted to carry out the following method steps:

a hydrofluoric acid recovery process consists of three steps which is formed in the dry vapor phase reaction according to any one of claims 1 and 2,

wherein the first step is extraction and distillation for separating anhydrous hydrogen fluoride from dilute hydrofluoric acid by extraction using concentrated sulfuric acid,

wherein the second step is concentration of diluted sulfuric acid, which is formed in above mentioned extraction and distillation step, by evaporation of diluted hydrofluoric acid and concentrated sulfuric acid is refused in the first step, and

wherein the third step is refining distillation of diluted hydrofluoric acid, which is formed in the second step, to separate to azeotropic hydrofluoric acid is feed to the first step; and a fluorine fixing step for water containing a trace amount of hydrofluoric acid, which formed in third step, to form granular calcium fluoride by reacting with granular calcium carbonate.

5. A fluorine fixing process for forming granular calcium fluoride, wherein hydrogen fluoride, which is formed in a waste liquor disposal step by liquefying off-gasses discharged from the dry vapor-phase reaction step, hydrofluoric acid recovery step, and condensers installed in the dry vapor-phase reaction, or hydrogen fluoride formed in

the dry vapor-phase reaction step, the off-gases thereof and the waste liquid are mixed and the mixture is allowed to contact granular calcium carbonate.

6. A method for processing depleted UF_6 in which the first and second fluidized bed reactors are plate type fluidized bed reactors each having a plurality of chambers, comprising:

a dry vapor-phase reaction step for forming U_3O_8, hydrogen fluoride and oxygen at reaction temperatures of the first fluidized bed reactor and second fluidized bed reactor of 230 to 280°C and and 600 to 700°C, respectively; and

a fluorine fixing step for forming granular calcium fluoride by allowing hydrogen fluoride generated in said dry vapor-phase reaction step to react with granular calcium carbonate at a temperature of 150 to 300°C.

7. A method for processing depleted UF_6 according to Claim 6, wherein a dilute aqueous hydrogen fluoride solution formed in the fluorine fixing step is used for the steam to be used in the dry vapor-phase reaction step.

8. A method for processing depleted UF_6 comprising:

three steps for hydrofluoric acid recovery which is formed in the dry vapor phase reaction according to any one of claims 1 and 2,

wherein the first step is extraction and distillation for separating anhydrous hydrogen fluoride from dilute hydrofluoric acid by extraction using concentrated sulfuric acid,

wherein the second step is concentration of diluted sulfuric acid, which is formed in above mentioned extraction and distillation step, by evaporation of diluted hydrofluoric

acid and concentrated sulfuric acid is refused in the first step, and

wherein the third step is refining distillation of diluted hydrofluoric acid, which is formed in the second step, to separate to azeotropic hydrofluoric acid is feed to the first step; and a fluorine fixing step for water containing a trace amount of hydrofluoric acid, which formed in third step, to form granular calcium fluoride by reacting with granular calcium carbonate.

9. A depleted UF_6 processing plant comprising:

a first fluidized bed reactor having at least one plate and configured to react depleted UF_6 with steam at a temperature of 230 to 280°C and produce UO_2F_2 and hydrogen fluoride, the at least one plate forming a plurality of communicated chambers in the first fluidized bed reactor;

a second fluidized bed reactor having at least one plate, connected to the first fluidized bed reactor and configured to react the UO_2F_2 with steam at a temperature of 600 to 700°C and produce U_3O_8, hydrogen fluoride and oxygen, the at least one plate forming a plurality of communicated chambers in the second fluidized bed reactor; and

a fluorine fixing reactor including granular calcium carbonate and connected to the first and second fluidized bed reactors, the fluorine fixing reactor being configured to react the hydrogen fluoride generated in the first and second fluidized bed reactors with the granular calcium carbonate at a temperature of 150 to 300°C and produce granular calcium fluoride.

10. A depleted UF_6 processing plant according to claim 9, further comprising a condenser connected to the fluorine fixing reactor and configured to condense a gas discharged from the fluorine fixing reactor, wherein the condenser is communicated to the first and second fluidized bed reactors to recycle a dilute aqueous hydrogen fluoride solution produced in the condenser to a steam generator to form steam for use in the first and second fluidized bed reactors.

11. A depleted UF_6 processing plant according to claim 9 or 10, wherein the fluorine fixing reactor comprises a plurality of cylinders configured to exchangeably connect one after another to the first and second fluidized bed reactors.

12. A depleted UF_6 processing plant according to any one of claims 9 to 11, further comprising a cooling device connected to the first and second fluidized bed reactors and configured to cool down the hydrogen fluoride produced in the first and second fluidized bed reactors to 150 to 300°C.

13. A depleted UF_6 processing plant according to any one of claims 9 to 12, wherein the first and second fluidized bed reactors each have the plurality of communicated chambers vertically partitioned by the at least one partition plate.

14. A method for processing depleted UF_6, comprising the steps of:

reacting the depleted UF_6 and steam at a temperature of 230 to 280°C in a first fluidized bed reactor having at least one plate and configured to react depleted UF_6 with steam to produce UO_2F_2 and hydrogen fluoride, the at least one plate forming a plurality of communicated chambers in the first fluidized bed reactor;

reacting the UO_2F_2 with steam at a temperature of 600 to 700°C in a second fluidized bed reactor having at least one plate and configured to react UO_2F_2 with steam to produce U_3O_8, hydrogen fluoride and oxygen, the at least one plate forming a plurality of communicated chambers in the second fluidized bed reactor; and

reacting the hydrogen fluoride generated in the first and second fluidized bed reactors with granular calcium carbonate in a fluorine fixing reactor at a temperature of 150 to 300°C to produce calcium fluoride.

15. A method for processing depleted UF_6 according to claim 14, further comprising:

condensing a gas discharged from the fluorine fixing reactor to produce a dilute aqueous hydrogen fluoride solution; and

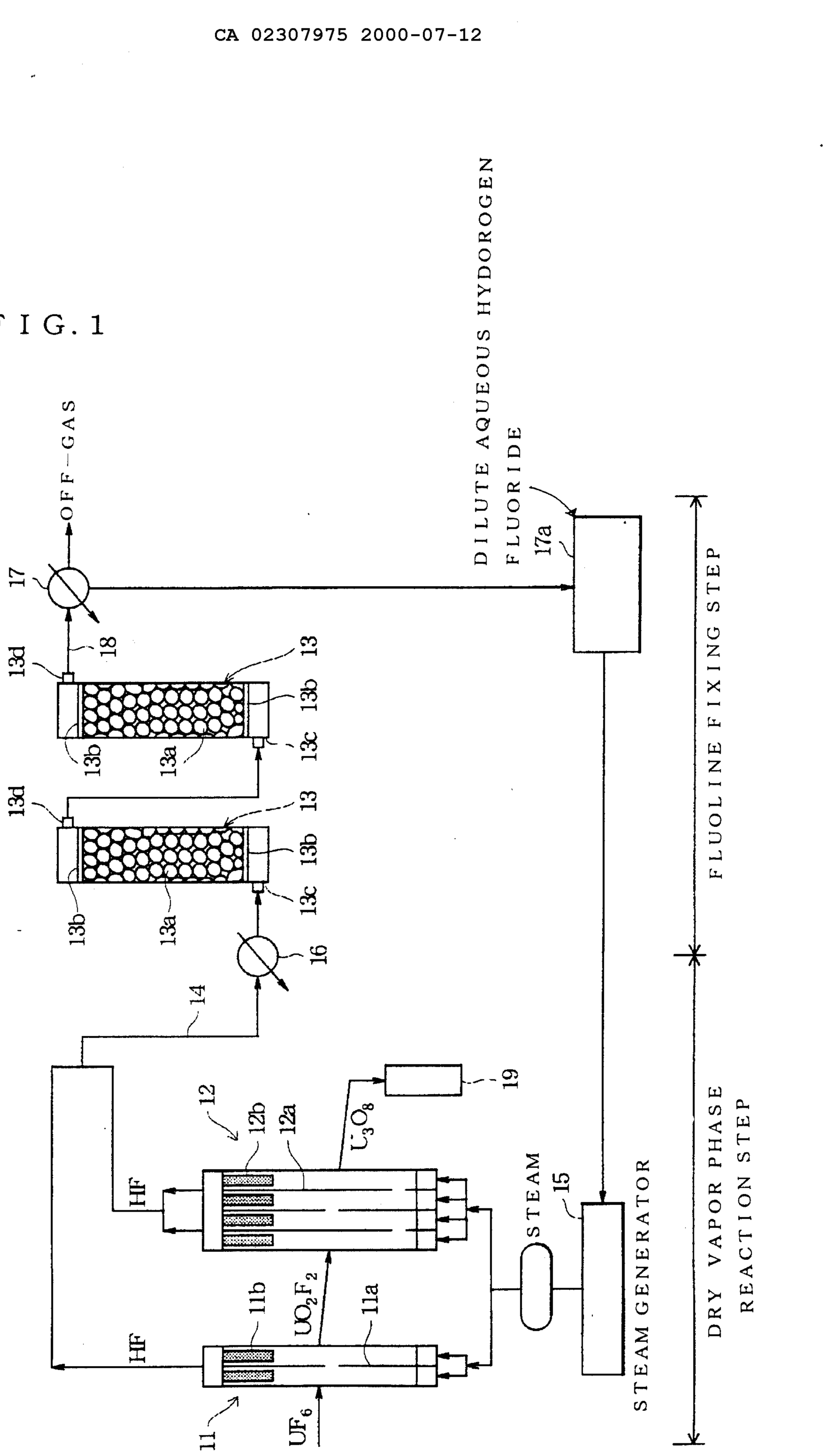
recycling the dilute aqueous hydrogen fluoride solution to a steam generator to form steam for use in the first and second fluidized bed reactors.

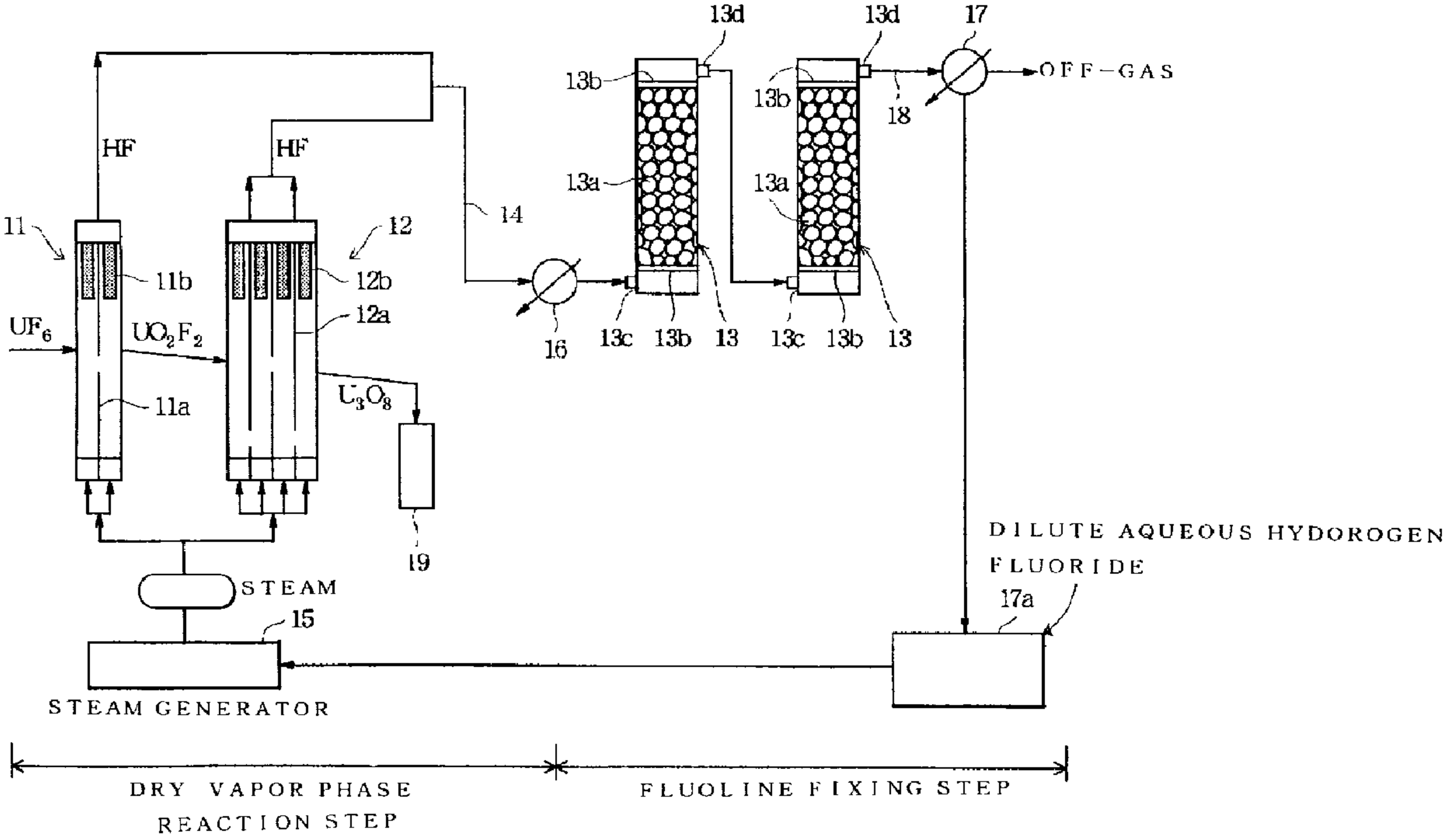
16. A method for processing depleted UF_6 according to claim 14 or 15, wherein the calcium fluoride produced in the reacting step of the hydrogen fluoride and granular calcium carbonate is in a form of granules.

17. A method for processing depleted UF_6 according to any one of claims 14 to 16, wherein the reacting steps of the depleted UF_6 and steam, and the UO_2F_2 and steam comprise a dry vapor phase reaction.

18. A depleted UF_6 processing plant according to any one of claims 9 to 13, wherein the granular calcium carbonate in the fluorine fixing reactor comprises calcium carbonate granules having a grain size of 350 to 800 μm.

FIG. 1


DRY VAPOR PHASE FLUORINE FIXING STEP
REACTION STEP
STEAM GENERATOR
STEAM
15
19
U_3O_8
12
12b
12a
HF
UO_2F_2
11b
11a
HF
11
UF_6
F_2
14
16
13d
13
13b
13c
13a
18
17
OFF-GAS
DILUTE AQUEOUS HYDOROGEN FLUORIDE
17a


HF
HF
11
12
11b
12b
12a
UF6
UO2F2
U3O8
11a
19
14
16
13d
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17
OFF-GAS
13b
13b
18
13a
13a
13c
13b
13
13c
13b
13
STEAM
15
STEAM GENERATOR
DILUTE AQUEOUS HYDOROGEN FLUORIDE
17a
DRY VAPOR PHASE REACTION STEP
FLUOLINE FIXING STEP