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(54) Title: PREPARATION OF CALCIUM SILICATE AND SULFUR DIOXIDE

(57) Abstract: Calcium fluoride is converted to hydrofluoric acid and a calcium silicate aggregate by reaction with silica and partially dissociated steam at elevated temperatures.

PREPARATION OF CALCIUM SILICATE AND SULFUR DIOXIDE

Background

United States Patent 2,232,099 (de Jahn) indicates that carbon is needed to reduce phosphogysum, but he recognized that silica would work only if alumina were present.

United States Patents 2,687,946 and 4,687,947 (Manning) similarly teach that carbon is an essential component for the subject process.

Summary of the Invention

Sulfur dioxide (SO_2) is released and recovered from calcium sulfate ($CaSO_4$) while generating a usable, environmentally friendly by-product, calcium silicate ($CaSiO_x$). A stochiometric amount of $CaSO_4$ particles is admixed with silica (SiO_2), e.g. in the form of sand, waste by-products, etc., and then introduced into a fuel-fired kiln.

Feeding water vapor into the kiln is critical to making the process work correctly. The water vapor is partially dissociated into nascent hydrogen (H^0) and nascent oxygen (O^0) at an elevated temperature in the kiln. The water vapor for the process is supplied by either direct water sprays or by steam injection.

At the elevated temperature of the kiln, the SiO_2, H^0 and O^0 react with the $CaSO_4$ to form $CaSiO_x$ and released SO_2 vapor. The SO_2 vapor exits the kiln in a discharge gas stream and is captured and recovered as sulfuric acid (H_2SO_4) in a typical commercially available tail-gas absorption/recovery unit, similar to those used in smelter operations.

Once the $CaSiO_x$ is formed, it passes through the kiln and is discharged and transported to outside storage stacks. As the $CaSiO_x$ is tumbled inside the hot kiln, it tends to granulate into mostly smooth particles that have a glass-like coating on the

outside. All impurities that were contained in the $CaSO_4$ are trapped inside the glass-like coating. Depending upon the impurities in the $CaSO_4$, the glass-like coating can effectively prevent/reduce release of objectionable gaseous elements, such as radon. The $CaSiO_x$ particles are essentially insoluble and can be safely and effectively utilized for construction fill material, such as roadways, or as aggregate in cement. If the material is not sold, it can be stored in outside stacks that are environmentally friendly.

Brief Description of the Drawing

Figure 1 is a process flow diagram illustrating an embodiment of the invention.

Details

Phosphogypsum, gypsum or any other calcium sulfate is fed to a kiln heated to about 2800°F (from 2200°, preferably 2500°, to 3000°F), and water is added to cool formed clinker or aggregate and also is vaporized and dissociates (2 to 5% dissociation) as it traverses the kiln. The dissociated nascent hydrogen and oxygen react with the silicon dioxide to form H_2SiO_x (silicious or silicic acid) where X is 3 or 4. This occurs to the silica phosphogypsum mixture fed to the kiln. The nascent hydrogen and nascent oxygen react with the silica to form silicious acid. The calcium sulfate reacts with the silicious or silicic acid under the high temperature (2200° to 2900°F) and forms a crystalline/glasslike insoluble calcium silicate and releases sulfur dioxide gas. The sulfur dioxide (SO_2) gaseous emission is reclaimed , e.g., in a conventional sulfuric acid plant, producing sulfuric acid (98%).

With reference to Figure 1 and Table 1, phosphogypsum or gypsum (line #1) is fed to a mixing chamber where it is thoroughly mixed with a stream of silica (line

#2). The mixture is optionally granulated or pelletized into a particle size that will make an efficient feed to the heated kiln. To help stick the materials together and form pellets, a binder may be used (line #3).

The pellets are then fed (line #4) to a gas, oil or coal-fired (line #8) kiln. A stream of water (in the form of either

Table 1
Description of Process Lines - $CaSO_4$ Regeneration

Line #	Material	Composition	Description
1	Calcium sulfate ($CaSO_4$)	50-100% $CaSO_4$	Filter cake from a phosphoric acid plant, mineral feed, etc.
2	Silica (SiO_2)	50-100% SiO_2	Sand, waste amorphous silica from aluminum manufacturing, etc.
3	Binder	Calcium ligno-Sulfonate or equivalent	An effective binder to facilitate the pelletizing or granulating of the calcium sulfate/silica mixture.
4	Mixture of $CaSO_4$ and SiO_2	≥ Stochiometric Ratio	Pelletized mixture of the calcium sulfate and silica prior to being fed to the kiln.
5	Water or Steam	H_2O at rate of up to 20 x stochiometric	Water spray or ~ 50 psig steam added through atomizing nozzles.
6	Mixture of combustion gas and SO_2	---	The exhaust gases from the kiln.
7	H_2SO_4 acid	5 to 10%	H_2SO_4 acid from the double contact acid train.
8	Natural gas, fuel oil, or coal	Standard	Heat source for kiln.
9	Clean air	nil % SO_2	Clean exhaust to the atmosphere from the sulfuric acid plant.
10	Calcium silicate solids	$CaSiO_x$ containing all of the impurities present in the calcium sulfate	Solids discharge from the kiln. To be used for cement clinker, construction fill, roadbed, etc.

water or steam) (line #5) is injected into the discharge end of the kiln. The steam dissociates in the kiln and supplies the hydrogen and oxygen necessary for the reaction to go to completion. Because only about 2 to 5 % of the steam dissociates readily, the amount of steam required is up to 20 times the stochiometric requirement.

The retention time in the kiln is about 2 to 4 hours; the optimum time is dependent on desulfurization of the clinker. The operating temperature for the kiln is about from 2200° to 2900°F.

Within the kiln, a reaction takes place; sulfur dioxide gas is liberated and a solid calcium silicate is formed. A rotary kiln is desirable, but not necessary, to allow insoluble calcium silicate to form into well-formed glassy pellets to facilitate their end use.

The sulfur dioxide gas exits the kiln with exhaust gases (line #6), and is recovered by a conventional double contact sulfuric acid plant which produces sulfuric acid at a concentration of up to 98% H_2SO_4 (line #7). A high temperature electrostatic precipitator may be required to insure a clean gas feed to the sulfuric acid unit.

Calcium silicate aggregate or clinker is formed during the reaction and is discharged from the end of the kiln (line #9). The produced calcium silicate aggregate or clinker contains essentially all of the impurities associated with the employed calcium sulfate, e.g. those in original phosphate rock from which phosphogypsum is derived. The calcium silicate takes on a glassy form and tends to encapsulate the impurities within an essentially inert shell. This inert material can then be safely utilized for construction fill, cement clinker, roadbeds, etc.

Whenever "about" appears in the disclosure or claims, a range of ± 5% is contemplated unless otherwise indicated.

The term "nascent" is a term used to describe the abnormally active condition of an element. In the case of a diatomic element (such as H_2 or O_2), it can exist in a monatomic state and be highly reactive, for example H^0 or O^0. The high temperature in the kiln creates the conditions for this phenomenon to occur which then results in the reaction mechanisms described.

The invention and its advantages are readily understood from the preceding description, and it is apparent that various changes may be made in the process and products without departing from the spirit or scope of the invention or sacrificing its material advantages. The process and products hereinbefore described are merely illustrative of preferred embodiments of the invention.

WHAT IS CLAIMED IS:

1. A method for producing calcium silicate and sulfur dioxide which comprises reacting a mixture of calcium sulfate and silica with dissociated nascent hydrogen and nascent oxygen at a temperature in the range of from about 2500° to about 3000°F (about 1371° to about 1649°C).

2. A method of claim 1 which consists essentially of reacting a mixture of calcium sulfate and silica with dissociated nascent hydrogen and nascent oxygen at a temperature in the range of from about 2200° to about 3000°F (about 1204° to about 1649°C).

3. A method of claim 1 which comprises reacting the mixture in the absence of carbon and/or alumina.

4. A method of claim 1 wherein the temperature range is from about 2500° to about 3000°F (about 1371° to about 1649°C).

5. A method of claim 1 wherein the temperature range is from about 2200° to about 2900°F (about 1204° to about 1593°C).

6. A method of claim 1 wherein the temperature is about 2800°F (about 1538°C).

7. A method of claim 1 wherein the calcium sulfate is in the form of gypsum or phosphogypsum.

8. A method of claim 1 wherein, prior to reacting, the mixture of calcium sulfate and silica is granulated or pelletized.

9. A method of claim 8 wherein said mixture is combined with a binder.

10. A method of claim 1 which is conducted in a rotary kiln.

11. A method of claim 1 which is conducted in a kiln from which sulfur dioxide is discharged in gaseous form and calcium silicate clinker or aggregate is discharged in a crystalline/glasslike insoluble form.

12. A method of claim 11 wherein the calcium sulfate is in phosphogypsum form containing impurities, and discharged calcium silicate aggregate or clinker encapsulates the impurities within an essentially inert shell.

13. A method of claim 1 which is conducted in a kiln in which introduced water and/or steam is partially dissociated into nascent hydrogen and nascent oxygen.

14. A method of claim 13 wherein the water or steam is up to 20 times the stochiometric requirement.

15. Calcium silicate aggregate or clinker in a glassy form which encapsulates within an essentially inert shell impurities associated with calcium from which the calcium silicate was derived.

AMENDED CLAIMS

[received by the International Bureau on 26 February 2002 (26.02.02);
original claims 1 and 2 amended; remaining claims unchanged (1 page)]

1. A method for producing calcium silicate and sulfur dioxide which comprises reacting a mixture of calcium sulfate and silica with dissociated nascent hydrogen and nascent oxygen at a temperature in the range of from about 2200° to about 3000°F (about 1204° to about 1649°C).

2. A method of claim 1 which consists essentially of reacting a mixture of calcium sulfate and silica with dissociated nascent hydrogen and nascent oxygen at a temperature in the range of from about 2200° to about 3000°F (about 1204° to about 1649°C).

3. A method of claim 1 which comprises reacting the mixture in the absence of carbon and/or alumina.

4. A method of claim 1 wherein the temperature range is from about 2500° to about 3000°F (about 1371° to about 1649°C).

5. A method of claim 1 wherein the temperature range is from about 2200° to about 2900°F (about 1204° to about 1593°C).

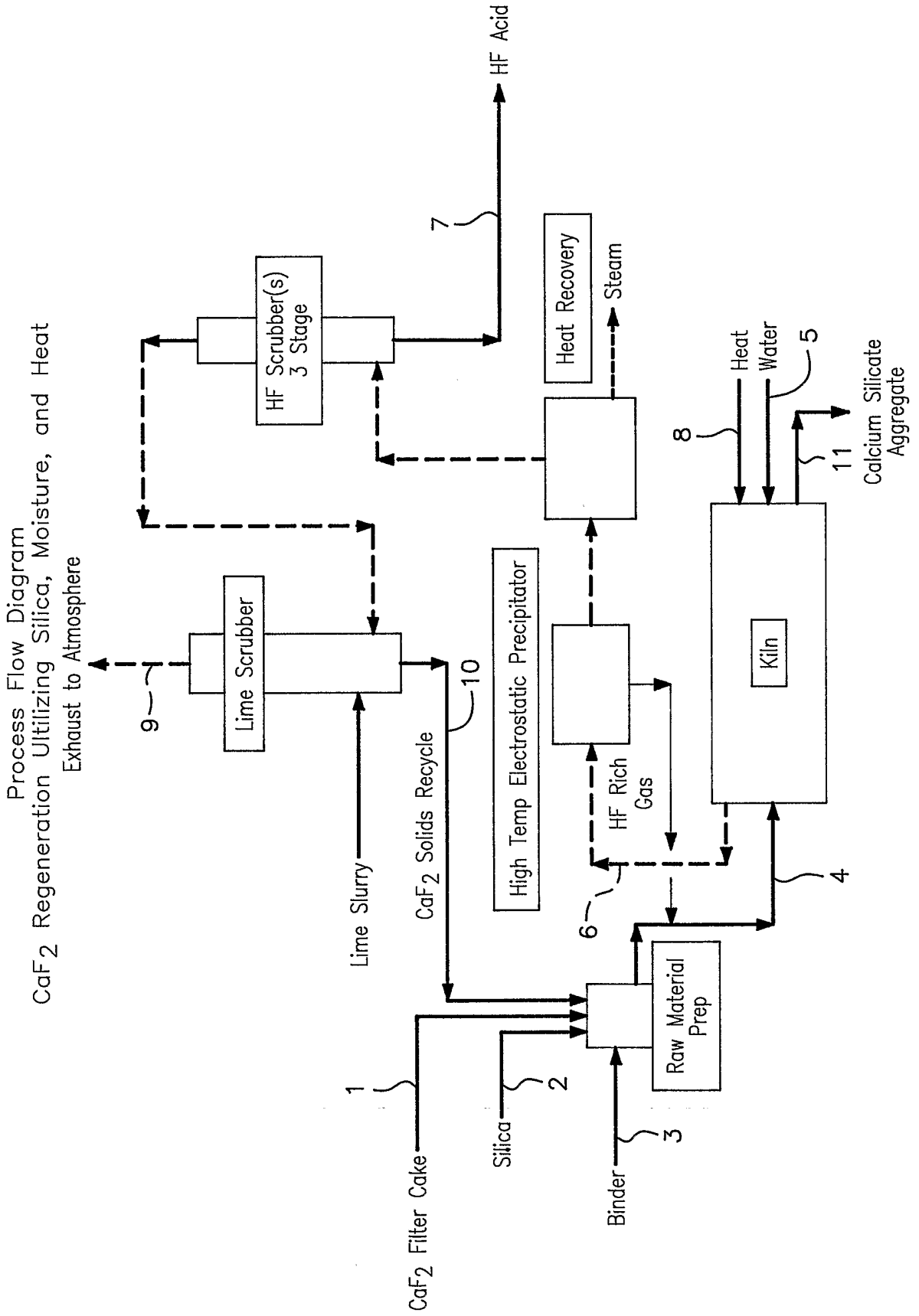
6. A method of claim 1 wherein the temperature is about 2800°F (about 1538°C).

7. A method of claim 1 wherein the calcium sulfate is in the form of gypsum or phosphogypsum.

8. A method of claim 1 wherein, prior to reacting, the mixture of calcium sulfate and silica is granulated or pelletized.

9. A method of claim 8 wherein said mixture is combined with a binder.

10. A method of claim 1 which is conducted in a rotary kiln.


Process Flow Diagram
CaF_2 Regeneration Utilizing Silica, Moisture, and Heat
Exhaust to Atmosphere
HF Acid
HF Scrubber(s) 3 Stage
Heat Recovery
Steam
Heat
Water
Calcium Silicate Aggregate
Lime Scrubber
High Temp Electrostatic Precipitator
Kiln
HF Rich Gas
Lime Slurry
CaF_2 Solids Recycle
Raw Material Prep
CaF_2 Filter Cake
Silica
Binder
1
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/31053

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 33/24
US CL : 423/331

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 423/331, 541.1, 539, 155, 178, 243.08, 244.02, 244.07, 651

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,312,842 A (WILSON, SR. et al.) 26 January 1982 (26.01.1982), column 4, lines 36-39; column 4, lines 64-67.	1-15
A	US 4,415,543 A (WILSON, SR. et al.) 15 November 1983 (15.11.1983), abstract	1-15
A	US 4,075,284 A (JOHNSON) 21 February 1978 (21.02.1978), abstract	1-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2001 (21.11.2001)	28 DEC 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Steven P. Griffin Telephone No. 703-308-0661

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