

DESCRIPTION**PRODUCTION PROCESS OF HIGH-PURITY GYPSUM****5 Technical Field**

 This invention relates to a process for the production of high-purity gypsum which does not contain much impurities. More specifically, the present invention is concerned with a process for producing high-quality gypsum having low impurity
10 content and high whiteness, especially crystals of dihydrate gypsum by having a calcium source such as limestone sufficiently dissolved as a calcium salt with a mineral acid in a water phase, removing impurities in the calcium source as undissolved residue, and then reacting the calcium salt with sulfuric acid
15 to form and crystallize gypsum.

Background Art

 Gypsum is widely used not only as building materials but also in a variety of fields. In each application field, gypsum
20 is obviously required to have quality and properties specific to the application field. Especially in the fields of molding materials and dental applications, gypsum is not acceptable if it contains impurities and presents a brown to dark gray color due to the impurities, and high-purity gypsum having high
25 whiteness is required. In these application fields, gypsum

crystals large in particle size and small in aspect ratio are needed because cast gypsum products are required to have high mechanical strength.

So-called natural gypsum which is available from a natural mineral, however, includes practically no product capable of satisfying these requirements, and most of natural gypsum contains impurities such as iron, aluminum and/or silica at high levels. Therefore, a variety of attempts have been made to date with a view to developing a method, apparatus or process for the production of gypsum having low impurity contents. As a representative example, there is a process for producing gypsum by adding water to lime powder to form a slurry and reacting the lime with sulfuric acid in a predetermined pH range.

Even with such conventional production processes of gypsum, however, it is still difficult to meet the above-described requirements, because a calcium source employed as a starting material, such as limestone or lime, contains iron, silica, magnesium and the like as impurities and these impurities remain as sparingly soluble reaction products with sulfuric acid, as are in unreacted forms, or in some instances, together with an unreacted portion of the calcium source in the resulting gypsum, thereby rendering the gypsum to have high impurity contents. As a corollary to this, it has been needed to produce gypsum by using limestone of low impurity contents

or calcium carbonate, which was prepared in advance with low impurity contents, as a starting material, resulting in the circumstance that the production cost of gypsum unavoidably becomes high.

5 Moreover, the gypsum obtained as described above is generally in the form of fine needle-like crystals, and calcined gypsum which is obtained by calcining such gypsum requires mixing water in an increased amount upon its use. A cast product available from a gypsum slurry having a large mixing water
10 content is accompanied by problems in quality such as lowered strength.

 Accordingly, an object of the present invention is to make it possible to produce gypsum, which has high whiteness and low impurity contents, at low cost even when a calcium source having
15 high impurity contents is used as a starting material. Another object of the present invention is to provide gypsum large in crystal size and small in aspect ratio, especially crystals of dihydrate gypsum.

20 Disclosure of the Invention

 The above-described objects can be achieved by the present invention to be described hereinafter. Specifically, the present invention provides a process for the production of high-purity gypsum, which comprises reacting a calcium source,
25 as a starting material, with a mineral acid in a water phase

to have the calcium source sufficiently dissolved as a calcium salt in the water phase, separating and removing undissolved residue from a resulting water phase, adding sulfuric acid to a water phase, which has been obtained by the removal of the undissolved residue, to crystallize gypsum, and separating the crystallized gypsum from the water phase.

Brief Description of the Drawings

FIG. 1 is a flow sheet showing facilities or a plant suitable for use in the practice of the process of the present invention for the production of gypsum.

Best Modes for Carrying Out the Invention

The present invention will hereinafter be described in further detail based on preferred embodiments.

[Starting material]

Calcium sources usable in the present invention are commonly known, and include a wide variety of calcium compounds which are available from natural minerals or are produced industrially. Specific examples of such calcium compounds can include natural calcium carbonate sources such as limestone, marble, calcite and aragonite; slaked lime; quick lime; and light calcium carbonate in various crystalline forms, which can be industrially obtained by injecting carbon dioxide gas into a milk of lime. In the present invention, these calcium

carbonate sources can be used either singly or in combination.

No particular limitation is imposed on the particle size of the calcium source. Calcium sources in a wide range of particle sizes, ranging from fine powder to particles, can each
5 be used as a starting material in the present invention. It is also possible to form a powdery or particulate calcium source into a pellet-like or granular calcium source by a suitable method such as granulation. Depending on the particle size of the calcium source, the scale and operation conditions of
10 facilities for use in the present invention should be modified.

The present invention has a merit in that the cost of the starting material for gypsum to be obtained can be lowered, as a low-purity calcium compound with silica, iron, aluminum and the like contained as impurities in substantial amounts can be
15 used as a starting material.

In general, these calcium sources have properties such that they have low solubility in water but are readily soluble in a mineral acid, such as hydrochloric acid or nitric acid, to form solutions of water-soluble calcium salts. The present
20 invention, therefore, makes use of a mineral acid for the dissolution of the calcium source exemplified as described above. As such a mineral acid, one having high purity is not needed but one of general industrial grade is sufficient. Further, waste mineral acids which occur in various chemical
25 industry and semiconductor industry can also be used suitably.

No particular limitation is imposed on the mineral acid to be used in the present invention, and its concentration can be determined in relation to a production size at the stage of designing of a plant or facilities for the practice of the present invention.

Upon actually operating facilities or a plant, the flow rate of the mineral acid can be controlled by an unillustrated flow meter or solenoid valve arranged in a feed line of the mineral acid in a plant such as that shown in FIG. 1. Such a mineral acid may be temporarily stored in a reservoir 4.

As a supply source of sulfate ions upon crystallization of gypsum crystals in the present invention, sulfuric acid is suitable. No particular limitation is imposed on the concentration of sulfuric acid, and desired one of sulfuric acids the concentrations of which vary widely can be used in view of various factors such as the kinds and contents of impurities in the starting material and the residence time of a water phase in crystallization of gypsum to be described subsequently herein.

In the present invention, high-purity gypsum can be produced by the above-described facilities or plant no matter whether the operation is batchwise or continuous. The operation mode of above-described facilities or plant can be freely determined in view of the application field, required quality and economy of the high-purity gypsum available from

the present invention.

The present invention will hereinafter be described more specifically with reference to FIG. 1. The following is a specific embodiment of the present invention, in which

5 hydrochloric acid is used as a mineral acid, calcium carbonate is used as a calcium source, and crystals of dihydrate gypsum are produced.

[Dissolution of calcium carbonate]

No particular limitation is imposed on the manner of
10 addition of calcium carbonate, water and hydrochloric acid. For example, subsequent to mixing of calcium carbonate with water, hydrochloric acid may be added to react calcium carbonate with hydrochloric acid. As an alternative, hydrochloric acid and water may be firstly mixed to form an aqueous solution of
15 hydrochloric acid, said aqueous solution having an appropriate concentration, and powdery or particulate or aggregated calcium carbonate may then be added to the aqueous solution of hydrochloric acid to react them together. As one example of such an embodiment, FIG. 1 illustrates process steps in which
20 calcium carbonate is mixed beforehand with water to prepare a slurry 1, the slurry 1 is stored in a calcium carbonate slurry reservoir 2, from which the slurry 1 is fed into a dissolver tank 3 by a suitable means such as a pump P, and on the other hand, hydrochloric acid is fed from the hydrochloric acid
25 reservoir 4 to the dissolver tank 3, in which calcium carbonate

and hydrochloric acid are reacted. The concentration of the calcium carbonate in the slurry 1 can be set as desired in view of the operation conditions and controllability of the plant.

The reaction between calcium carbonate and hydrochloric acid in the dissolver tank 3 can be expressed by the following chemical reaction formula:



When the pH of the water phase is in the acidic range in the above reaction, the dissolving and neutralizing reaction of calcium carbonate with hydrochloric acid proceeds promptly. When the pH is around the neutral, the reaction is retarded. In the alkaline range, on the other hand, the reaction does not proceed and unreacted calcium carbonate remains. It is, therefore, necessary to have the calcium carbonate dissolved as much as possible in the acidic range and then to add calcium carbonate and/or its slurry to the water phase such that the eventual pH of the water phase is adjusted to fall within a preferred range.

The pH of the water phase in the dissolver tank 3 may preferably be in a range of from 2 to 6, with a range of 3 to 5 being desired. At a pH lower than this range, the dissolving reaction of calcium carbonate is promoted, leading to an improvement in the yield of crystals of dihydrate gypsum as a final product. On the other hand, however, impurities such as iron are allowed to dissolve in the water phase, eventually

resulting in colored crystals of dihydrate gypsum with lowered purity and insufficient crystal growth. At a pH higher than the above range, on the other hand, the impurities can be removed, but the dissolving reaction of calcium carbonate is retarded, calcium carbonate remains in the unreacted form, and as a result, the calcium carbonate is required in a greater amount for the formation of dihydrate gypsum.

The reaction and residence time of the reaction mixture in the dissolver tank 3 and the specification of the apparatus can be determined depending on the kind and particle size of calcium carbonate to be employed, the pH of the water phase during the reaction, the production capacity of the facilities or plant crystals for dihydrate gypsum, and the like. Further, the dissolver tank 3 may preferably be constructed of a material having corrosion resistance to hydrochloric acid and calcium carbonate used in the above-described reaction. It is also desired to arrange an agitator 5 in the tank such that the contents can be stirred evenly. No particular limitation is imposed on the specification of the agitator 5, and any agitator can be used insofar as it is generally employed.

In actual operation of the facilities or plant, the flow rate of the slurry and/or hydrochloric acid can be controlled depending on the liquid level of the water phase in the dissolver tank 3 or the pH of the water phase in the dissolver tank 3 by an unillustrated solenoid valve of flow meter arranged in the

feed line from the slurry reservoir 2 and/or hydrochloric acid tank 4 to the dissolver tank 3. As a result of the neutralizing and dissolving reaction, carbon dioxide gas 6 is produced. It is necessary to safely exhaust this gas out of the system by an unillustrated exhauster.

[Separation and removal of undissolved residue]

The water phase, which has been drawn out of the dissolver tank 3 and contains calcium chloride, is filtered by a solid-liquid separation means 7 such as a filter, whereby undissolved residue 8 contained in the water phase, such as iron and silica, is separated and removed. The residue 8 so separated and removed is discharged as sludge out of the system, and the water phase is fed to the subsequent step.

As this solid-liquid separation means 7, it is desired to adopt an appropriate apparatus or plant out of general centrifugal, pressure or vacuum filters in view of the purity of the starting material, the amount of the undissolved residue, the speed of the treatment, the residence time of the water phase in the dissolver tank 3, and so on. As the pH of the water phase is acidic, it is necessary to construct the solid-liquid separation means 7 with a material having corrosion resistance.

[Heating of the water phase]

In the present invention, the water phase from the above-described solid-liquid separation means 7 is fed to a crystallization tank 9, in which crystals of dihydrate gypsum

are formed. To promote the growth of crystals of dihydrate gypsum in the crystallization tank 9, it is preferred to set the reaction temperature between calcium chloride and sulfuric acid 10 in the water phase as high as possible. Under co-
5 existence of calcium ions and chlorine ions in the reaction system, the temperature of the water phase may preferably be set in a range of from 30 to 80°C, with a temperature range of from 40 to 75°C being desired. If the temperature is set higher beyond the above range, anhydrous gypsum is crystallized. At
10 a temperature lower than the above range, on the other hand, the growth of crystals of dihydrate gypsum becomes slower.

To achieve the above-described objects, it is desired to heat the water phase in advance by arranging an equalizing tank 11, which is provided with heating means 12, between the
15 above-described solid-liquid separation means 7 and the crystallizing tank 9, in which the subsequent step is to be conducted, or to heat the water phase by similar heating means in the crystallizing tank 9. No particular limitation is imposed on the heating means 12, and a general heating method,
20 for example, direct heating by steam injection, indirect heating with steam, electric heating or the like can be adopted.

Upon actual operation of the facilities or plant, an unillustrated flow meter and solenoid valve can also be arranged for the control of the process in the feed line between the
25 equalizing tank 11, which is provided with the heating means

12, and the crystallization tank 9 such that the flow rate of the water phase with calcium chloride contained therein can be controlled.

[Formation of crystals of dihydrate gypsum by feeding sulfuric acid]

Upon formation of crystals of dihydrate gypsum in the crystallizing tank 9, sulfuric acid 10 is desired as a supply source for sulfate ions as described above. Its concentration can be chosen as desired depending on the specification of the apparatus. A reaction in which crystals of dihydrate gypsum are formed upon addition of the sulfuric acid 10 to the heated water phase can be expressed by the following chemical reaction formula:



Gypsum is available primarily in three crystalline forms, that is, dihydrate, hemihydrate and anhydrite. Especially in the crystallizing reaction of gypsum in such a solution as described above, each crystalline form has its own stable region depending on salts concurrently contained in the water phase and the temperature condition of the water phase. To stably crystallize crystals of dihydrate gypsum, it is therefore necessary to maintain the concentrations of the above-described salts and the temperature condition of the water phase within stable regions for crystals of dihydrate gypsum. The reaction temperature of the water phase and the concentrations of

coexisting chlorine ions in the water phase for the formation of the crystals of dihydrate gypsum may desirably be maintained in the following ranges from the standpoint of the formation and growth of crystals of dihydrate gypsum in the

5 crystallization tank 9.

To promote the growth of crystals of dihydrate gypsum, it is desired to set the reaction temperature high as described above. However, the higher the reaction temperature, the greater the solubility of the formed crystals of dihydrate
10 gypsum in the water phase and hence, the lower the yield of crystals of dihydrate gypsum. It is therefore desired to set the reaction temperature at a high temperature within a range in which resulting crystals of dihydrate gypsum are allowed to grow while retaining the form of dihydrate.

15 With the foregoing in view, it is desired to maintain the reaction temperature in the crystallizing tank 9 within a range of from 30 to 80°C, preferably within a range of from 40 to 75 and further, to control the total concentration of chlorine ions in the water phase at 5 to 15 wt.%. If the reaction temperature
20 or the total chlorine ion concentration is maintained high beyond the above-described temperature or concentration range, the water phase is a stable region for anhydrous gypsum, so that anhydrous gypsum is allowed to crystallize and further, is hardly allowed to remain as dihydrate during crystal growth.

25 If the reaction temperature of the total chlorine ion

concentration is set lower than the above-described range, fine needle-like crystals of dihydrate gypsum are formed, crystals of dihydrate gypsum can hardly be obtained with desired size and shape even if the residence time is set long.

5 On the other hand, as the residence time of the water phase in the crystallizing tank 9 is set longer under the above-described conditions, thick crystals of dihydrate gypsum are obtained with an increased particle size. It is, therefore, preferred to hold the water phase for about 0.5 to 12 hours or
10 so in the crystallizing tank 9. Crystals of dihydrate gypsum are, for example, in a fine needle-like form with an aspect ratio of from 10 to 20. By setting the residence time at several hours or so, coarse (plate-like or short prism-like) crystals having, for example, a thickness of approx. 100 μ m in
15 minor axis diameter can be obtained. Accordingly, the residence time should be determined in view of the application and required quality of crystals of dihydrate gypsum to be obtained.

 The concentration of solids (crystals of dihydrate
20 gypsum) in the crystallizing tank 3 may preferably be in a range of from 5 to 30 wt.%, with a range of from 10 to 25 wt.% being desired. A solid concentration lower than 5 wt.% cannot form crystals of dihydrate gypsum in a large amount in a single cycle of step, and is disadvantageous from the standpoint of
25 production cost. A solid concentration higher than 30 wt.%,

on the other hand, leads to a reduction in the below-described washability of the crystals with water and hence to inclusion of more impurities in crystals of gypsum to be obtained eventually. Solid concentrations outside the above range are, therefore, not preferred.

As has been described above, the crystals of dihydrate gypsum formed in the crystallizing tank 9 are in a fine needle-like form in the beginning of the crystallizing reaction, and in the course of the subsequent crystal growth, the setting of a long residence time in the crystallizing tank 9 makes it possible to obtain thick crystals of dihydrate gypsum. To readily control the crystals to plate-like or short prism-like crystals having a still smaller aspect ratio and a still greater thickness, a known habit modifier 18 or a crystal habit regulator can be added concurrently with sulfuric acid to the crystallizing tank 9.

Usable examples of such a habit modifier can include organic carboxylic acids, such as citric acid, maleic acid, succinic acid and sulfosuccinic acid, and salts thereof; water-soluble alkali metal salts of fatty acids such as palmitic acid, linoleic acid, ricinolic acid and glycolic acid; and alkylsulfonate salts, alkylbenzenesulfonate salts, and salts of the sulfate esters of higher alcohols. Particularly preferred are alkali metal dodecylbenzenesulfonates, especially, the sodium salt.

Whichever habit modifier is used, its amount can be set at about 5,000 ppm or lower based on the water phase although its effects on the growth of crystals of dihydrate gypsum vary from one habit modifier to another. When sodium dodecylbenzenesulfonate is used as a habit modifier, it can be added to at a concentration of about 500 ppm or lower, desirably from 5 to 100 ppm, more desirably from 5 to 50 ppm based on the water phase. Addition of sodium dodecylbenzenesulfonate at a concentration higher than the above range is not observed to bring about any additional effect on the growth of resulting crystals of dihydrate gypsum, because its habit-modifying effect is saturated. Use of such a habit modifier makes it possible to obtain plate-like or short prism-like crystals of dihydrate gypsum having an aspect ratio of from 2 to 4.

Insofar as crystals of dihydrate gypsum can be formed, it is necessary to promote the growth of crystals under high temperature conditions. Use of such high temperature condition, on the other hand, is accompanied by a problem in that due to an increase in the solubility of the crystals in the water phase, the yield of crystals of dihydrate gypsum may be lowered. To overcome this problem, it is desired to arrange the crystallizing tank in the form of two or more tanks, to connect these crystallizing tanks in series, to draw a water phase with the formed crystals of dihydrate gypsum therein out of the first crystallizing tank, to feed the water phase to the

second and subsequent crystallizing tanks, and then to hold the water phase under stirring in the tanks to subject the crystals to aging.

FIG. 1 illustrates a case in which two crystallizing tanks 9,9' are connected in series. Differentiation in temperature between a water phase in the second crystallizing tank (aging tank) 9' and a water phase in the first crystallizing tank 9 within the above-described temperature range of the water phase makes it possible to achieve an improvement in the yield of crystals of dihydrate gypsum. Described specifically, the dissolution of dihydrate gypsum in the water phase can be minimized by crystallizing dihydrate gypsum under a high water phase temperature condition in the first crystallizing tank 9 and setting the temperature of the water phase in the subsequent aging tank 9' lower than the above-mentioned temperature to lower the solubility of dihydrate gypsum. In this case, the aqueous solution of calcium chloride and the sulfuric acid can be fed all together to the first crystallizing tank 9 or can be fed in portions to the individual tanks 9,9'.

At the stage of designing facilities or a plant, it is necessary to keep in mind that the single or two or more crystallizing tanks 9,9' should not permit precipitation of coarse crystals of formed dihydrate gypsum and should assure prompt spreading of sulfuric acid into the water phase. Further, to evenly induce the crystallizing reaction for the formation

of crystals of dihydrate gypsum, crystallizing tanks 9,9' each of which is internally provided with a stirring blade 5 and radial baffles or draft tubes can be suitably employed. Further, the tanks 9,9' and the like may be constructed preferably with a material having corrosion resistance to hydrochloric acid.

When it is necessary to dilute concentrated sulfuric acid upon actual operation of the facilities or plant, an unillustrated diluting tank can be arranged additionally. It is also desired to arrange an unillustrated solenoid valve and flow meter, which have acid resistance, in the feed line of sulfuric acid and to control the flow rate of sulfuric acid. [Separation of crystals of dihydrate gypsum]

The water phase, which contains crystals of dihydrate gypsum aged as a result of the holding of the water phase as described above, is subjected to solid-liquid separation in a solid-liquid separator 13 such as a filter, whereby crystals 14 of dihydrate gypsum are separated and collected. Upon solid-liquid separation, thickened or plate-like or short prism-like crystals of dihydrate gypsum can be more easily collected by filtration. The filtered crystals of dihydrate gypsum are washed with washing water 15 and/or are regulated in pH (not shown) and are then dried, whereby the crystals 14 of dihydrate gypsum are obtained in a desired form. It is desired to conduct the water washing of the crystals of dihydrate gypsum at least once with water in an amount equal

to the amount of formed dihydrate gypsum. The washing effluent can be discharged out of the system through a suitable line 17 or can be returned to the dissolver tank 3. By this operation, the content of chlorine contained in the dihydrate gypsum can be lowered to 50 ppm or less. Incidentally, this washing can be performed in a manner known *per se* in the art, for example, by spraying.

The above-described pH regulation can be conducted by washing the crystals of dihydrate gypsum with an aqueous alkaline solution such as an aqueous solution of lime or by mixing the crystals of dihydrate gypsum again with water into slurry and washing the slurry with an aqueous solution of lime or a like solution.

A water phase (mother liquor) 16, which has been separated by the solid-liquid separation, is an aqueous solution of hydrochloric acid. In view of economy or the like, it is hence desired to recirculate the mother liquor 16 to the dissolver tank 3 and to reuse it for the dissolution of calcium carbonate. Reuse of the mother liquor 16 as described above makes it possible to efficiently perform continuous operation of the production process of the present invention by only replenishing a spent portion of hydrochloric acid with a fresh supply of hydrochloric acid. When the molar ratio of Cl/Ca is set, for example, at about 2 as in the above-described dissolving reaction, the amount of hydrochloric acid to be

replenished newly to the dissolver tank 3 is as little as about 20 wt.% of the mother liquor (aqueous solution of hydrochloric acid) 16 recirculated for reuse, thereby making it possible to achieve a reduction in the cost for the raw materials.

5 As the solid-liquid separator 13 in this step, any known solid-liquid separator, for example, a filter can be used in practice although use of a solid-liquid separator having acid resistance is preferred. In the above description, calcium carbonate and hydrochloric acid were used as preferred examples.

10 It is, however, to be noted that the present invention can also bring about similar results even when a calcium source other than calcium carbonate and a mineral acid other than hydrochloric acid are used.

15 **Examples**

 The present invention will hereinafter be described base on Examples. It should however be borne in mind that the present invention is not limited to the following Examples only.

Example 1

20 As a starting material, low-purity limestone powder was used. The followings are the results of its chemical analysis:

CaCO ₃	97.0 wt.%
SiO ₂	2.5 wt.%
MgO	0.3 wt.%

R_2O_3 0.2 wt. %
(R: Fe and/or Al)

The above-described limestone powder (618 g) was mixed and agitated with an equiamount of water into a 50 wt. % slurry, whereby a slurry of the limestone powder was obtained. The slurry was next poured together with hydrochloric acid (2,650 g), the concentration of which was 15 wt. %, into the dissolver tank 3. Under stirring, the limestone powder was dissolved in the hydrochloric acid so that a solution of calcium chloride was obtained. Carbon dioxide gas 6 which was produced in the course of the dissolution was exhausted out of the system by a local exhauster. The solution of calcium chloride was filtered by a line filter 7 to separate and remove undissolved residue 8, and the water phase was temporarily transferred to the equalizing tank 11 provided with the heating means 12. The dry weight of the undissolved residue 8 was 26 g.

The water phase in the tank 11 was then directly heated by steam injection such that its temperature was raised to 75°C. The water phase was then fed to the crystallization tank 9. As a habit modifier 18, sodium dodecylbenzenesulfonate was added such that its content reached about 35 ppm based on the amount of the liquid in the crystallization tank 9. At the same time, sulfuric acid 8 the concentration of which was 80 wt. % was also added such that its contents became approximately equal in equivalent to calcium ions in the water phase, followed by a

reaction under stirring for 6 hours. The liquid temperature was then lowered to 65°C, at which crystals of dihydrate gypsum were subjected to aging while holding the water phase there for 6 hours under stirring. The concentration of chlorine ions in the water phase during the aging was 10 wt.%. 5

The water phase with crystals of dihydrate gypsum contained therein was then filtered by filtration at the water-liquid separator 13, the crystals were washed with an equiamount of water, and the crystals of dihydrate gypsum were obtained. Properties of the crystals of dihydrate gypsum obtained after drying were investigated. The results are shown below. 10

	Crystal form	Plate-like crystals
	Purity	99.9%
15	Cl content	50 ppm
	Fe ₂ O ₃ content	10 ppm max.
	Whiteness (measured by Hunter's whiteness meter)	99%
	Minor axis diameter	150 m
20	Aspect ratio	2 to 4
	Bulk specific gravity	1.15

The crystals of dihydrate gypsum obtained as described above were then calcined into hemihydrate gypsum, and physical properties of the hemihydrate gypsum were investigated in

accordance with JIS R9101.

Spray mixing water amount 84%

Setting time

Initial setting time 4 minutes

5 Apparent final setting time 13 minutes 45 seconds

Final setting time 25 minutes

Maximum temperature 42.0°C

Wet tensile strength 11.5 kg/cm²

pH of cast product 6.9

10 It is evident from these results that the above crystals of dihydrate gypsum is sufficiently usable as calcined gypsum for a mold material or dental applications which is or are required to have a high degree of whiteness.

15 As the mother liquor 16 after the solid-liquid separation of the crystals 14 of dihydrate gypsum, it was possible to recover about 3 kg. The concentration of chlorine ions in the mother liquor 16 was 9.7 wt.% (10 wt.% based on hydrochloric acid), so that the mother liquor 16 was sufficiently usable for the dissolution of limestone powder in the first step.

20 Example 2

A similar test was conducted by using the mother liquor 16, which had been recovered as described above, likewise the hydrochloric acid employed in Example 1. Limestone powder in the same amount as in Example 1 was similarly formed into a slurry.

After the aqueous solution of hydrochloric acid (mother liquor) obtained in Example 1 was added to the slurry such that the aqueous solution of hydrochloric acid amounted to 20 wt.% of the weight of the slurry, the concentration of the slurry was adjusted to the same level as in Example 1, and a test was then conducted as in Example 1. As a result, the resultant crystals of dihydrate gypsum showed similar properties as in Example 1. Further, calcined gypsum obtained subsequent to calcination also had similar physical properties as the calcined gypsum obtained in Example 1.

Example 3

Further, the procedures of Example 2 were repeated 4 times additionally, that is, were repeated 5 time in total. The resultant crystals of dihydrate gypsum were tested as in Example 1. The crystals of dihydrate gypsum showed similar properties as in Example 1. Further, calcined gypsum obtained subsequent to calcination also had similar physical properties as the calcined gypsum obtained in Example 1.

Capability of Exploitation in Industry

According to the present invention, plate-like or short prism-like crystals of dihydrate gypsum of high purity, high whiteness, large bulk density and small aspect ratio can be efficiently obtained even when a low-purity calcium source is

used. Calcination of such crystals of dihydrate gypsum can also provide calcined gypsum of high purity, which is satisfactory in spray mixing water amount, setting time, and physical properties such as tensile strength.



CLAIMS

1. A process for the production of high-purity gypsum, which comprises reacting a calcium source with a mineral acid in a water phase to have said calcium source sufficiently dissolved as a calcium salt in said water phase, separating and removing undissolved residue from a resulting water phase, adding sulfuric acid to a water phase, which has been obtained by said removal of said undissolved residue, to crystallize gypsum, and separating said crystallized gypsum from said water phase.

2. A process according to claim 1, wherein said water phase which has been obtained by said removal of said undissolved residue is repeatedly used as said mineral acid to be reacted with said calcium source.

3. A process according to claim 1 or 2, wherein said calcium source is natural calcium carbonate, slaked lime, quick lime and/or an industrially produced calcium compound.

4. A process according to any one of claims 1-3, wherein said mineral acid is an acid having an anion capable of forming a water-soluble calcium salt, such as hydrochloric acid or nitric acid.

5. A process according to any one of claims 1-4, wherein hydrochloric acid is used as said mineral acid, and upon reaction of said calcium source with hydrochloric acid, said water phase has a pH of from 2 to 6.



6. A process according to any one of claims 1-5, wherein upon crystallization of gypsum, said water phase has a temperature of from 30 to 80°C.

7. A process according to any one of claims 1-6, wherein
5 hydrochloric acid is used as said mineral acid, and upon crystallization of gypsum, said water phase has a total chlorine concentration of from 5 to 15 wt.%.
10

8. A process according to any one of claim 1-7, wherein upon formation and crystallization of gypsum, an alkyl-
10 benzenesulfonate salt is used as a habit modifier.

9. A process according to any one of claims 1-8, wherein upon crystallization of gypsum, said gypsum is crystallized as crystals of dihydrate gypsum.