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(56) Documents cited
GB 1561269 **GB 0582749**
GB 1547422 **GB 0563019**

(58) Field of search
C1A

(54) Producing a -gypsum hemihydrate

(57) Gypsum hemihydrate in the α-form is made from gypsum dihydrate by heating an aqueous slurry containing gypsum dihydrate and a salt of sulfosuccinic acid (e.g. Mg salt) as the catalyst for crystallisation. The invention can be incorporated into a process for removing sulphur dioxide from exhaust gases.

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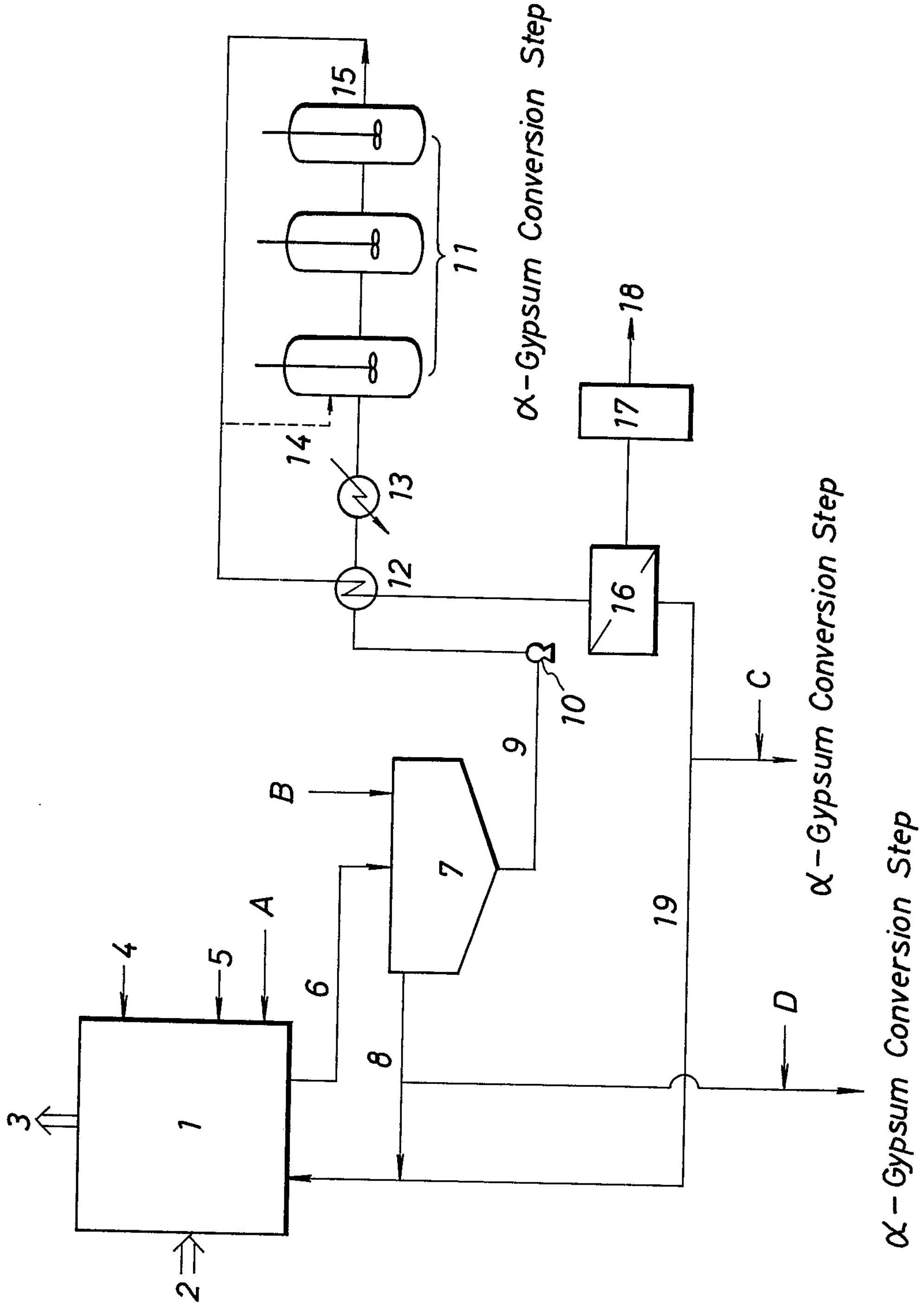
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α-Gypsum Conversion Step
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SPECIFICATION

Process for producing α-form gypsum hemihydrate

The present invention relates to a process for producing α-form gypsum hemihydrate (α-form calcium sulfate hemihydrate, hereinafter referred simply to as "α-gypsum").

α-gypsum at present is generally made by a wet process. In a liquid method conducted under saturated vapour pressure a slurry of gypsum dihydrate is dehydrated to convert the gypsum dihydrate into α-gypsum and the slurry is subjected to solid-liquid separation and drying, thus producing solid α-gypsum.

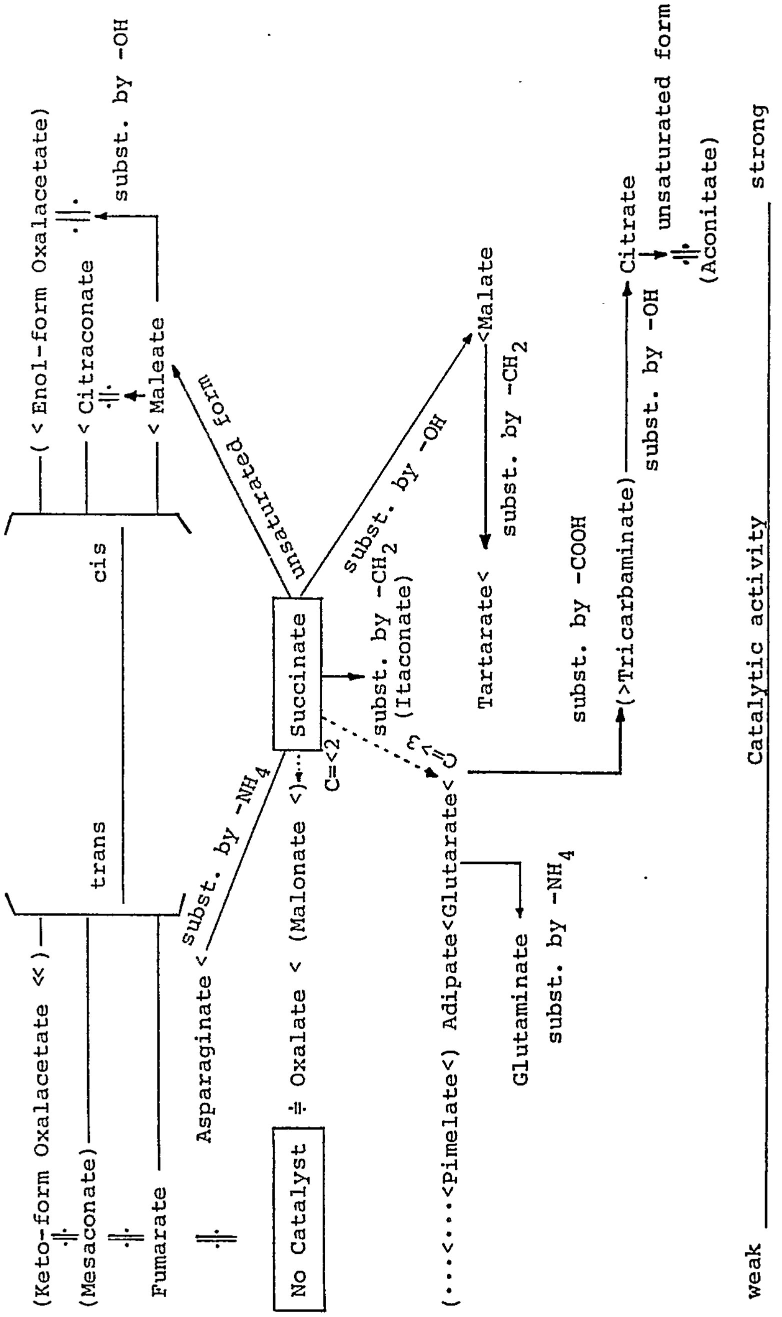
It is generally considered necessary, for the production of good quality α-gypsum, that the dehydration medium should comprise an aqueous solution of a substance which has a catalytic activity in crystallisation of α-gypsum as a catalyst for crystallisation. This can result in excellent quality α-gypsum which will contain a smaller mixing-water amount for normal consistency and the strength of shaped-articles of gypsum dihydrate obtained therefrom is large. It has been known that the aspect ratio of the crystals of such α-gypsum is ordinarily small and the bulk density thereof is large.

Hitherto, a large number of substances have been proposed as the catalyst for crystallisation. For instance, inorganic salts such as aluminium sulfate, magnesium sulfate, alums, etc. have been known as the catalyst for crystallisation (refer to Japanese Patent Publication No. 28-216 (1953) and Japanese Patent Application Laid-Open No. 55-162426 (1980), and as the organic catalyst for crystallisation, salts and amino-derivatives of higher fatty acids and sulfate-esters of higher alcohols, etc. (refer to Japanese Patent Publication No. 31-4375 (1956), water-soluble proteins such as keratin, casein, glues, etc. and salts of lower aliphatic polycarboxylic acids such as succinic acid, citric acid, etc. have been known.

Of the above-mentioned large number of catalysts for crystallisation, salts of lower aliphatic polycarboxylic acids represented by salts of succinic acid are considered to be most useful in industry from the viewpoints of the catalytic efficacy, the concentration in use and the price thereof.

Concerning the comparison of the catalytic activity of the above-mentioned salts of lower aliphatic polycarboxylic acids in "Liquid Methods under Saturated Vapor Pressure", M. Sekiya generally reported in the following of "SEKKO and SEKAI (Gypsum and Lime)", Vol. 51, page 55 (1961).

Comparison of Catalytic Activity of Salts of Lower Aliphatic Polycarboxylic Acids



(Note) The compound's name mentioned in the parenthesis are assumption.

Sodium succinate and sodium citrate (Japanese patent publication 57-25495, 1982) are used industrially but unfortunately are relatively expensive and so their use is hardly economic since α-gypsum is such a relatively cheap material.

Another problem is that it is considered undesirable for the α-gypsum to be contaminated with the catalyst, because of the risk of residual catalyst reducing the strength of shaped articles of gypsum dihydrated produced from α-gypsum. The α-gypsum therefore must be washed with water. The process therefore generates a large amount of water originating from the washing, the water adhered to the gypsum dihydrate and the water due to dehydration of the water of crystallisation. Handling this by-product water, especially if it is contamined with organic catalyst, creates treatment problems. Removal of the water by evaporation involves a large amount of heat energy.

It is not necessary to use any catalyst for crystallisation when producing β-form gypsum hemihydrate (hereinafter referred to as β-gypsum) and so it is only necessary to remove the adhered water of the gypsum dihydrate starting material and the water formed from the water of crystallisation on dehydration by heating. Accordingly, β-gypsum is obtained by simple operations in a low cost. However the physical properties of α-gypsum are inferior to β-gypsum but the relative cost of α-gypsum restricts use of the material to limited fields. It would be very desirable to be able to produce α-gypsum at a lower cost, and in particular at a cost close to β-gypsum.

It is known to try to achieve this object by combining the production of α-gypsum with the production of gypsum in the desulphurisation of exhaust gases.

There are two main ways of conducting such a process.

(i) A process wherein sulfur dioxide in an exhaust gas is directly converted into α-gypsum without producing gypsum dihydrate (refer to Japanese Patent Application Laid-Open No. 49-83695 (1974), Japanese Patent Publication No. 57-53292 (1982) and No. 57-49491 (1982).

(ii) A process wherein after converting sulfur dioxide in an exhaust gas is converted into gypsum dihydrate and the thus formed slurry containing gypsum dihydrate is converted into the slurry containing α-gypsum (refer to Japanese Patent Applications Laid-Open No. 53-50092 (1978), No. 55-113621 (1980), No. 56-129611 (1981).

For producing α-gypsum of the desired excellent quality, it is necessary to use a salt of dicarboxylic acid or tricarboxylic acid such as succinic acid, tartaric acid or citric acid as the catalyst for crystallisation in the system, and in the absence of such an organic catalyst for crystallisation, only α-gypsum of small bulk density is obtained.

The incorporation of such crystallisation catalysts in the absorbent liquid that is used for absorbing sulphur dioxide creates other problems in that the catalyst is liable to be decomposed during the oxidation of the sulphur dioxide or may inhibit this oxidation. Accordingly no commercially successful procedure is known in which the absorbing medium contains a suitable catalyst and is recirculated.

The overall process therefore requires an absorbent liquid for absorbing sulphur dioxide from the exhaust gas and a dehydration liquor containing an appropriate catalyst and at present it has not been possible satisfactorily to devise a single liquor that can serve for both purposes.

In a first aspect of the present invention there is provided a method for producing α-gypsum, comprising heating an aqueous slurry containing gypsum dihydrate and a salt of sulfosuccinic acid as the catalyst for crystallisation, thereby converting gypsum dihydrate into α-gypsum. The process conditions can be similar to those known for other liquid methods of making α-gypsum that are conducted under saturated vapour pressure, except that the novel catalyst is used.

When the sulphosuccinic acid is present as magnesium sulphosuccinic coprecipitation by sodium sulphate is effectively prevented and the liquid medium can be used for desulphurisation of an exhaust gas and the heat of the exhaust gas can be used to convert gypsum dihydrate (which may or may not be obtained solely from the sulphur dioxide in the exhaust gas) to α-gypsum.

In a second aspect of the present invention there is provided a method for producing α-gypsum, comprising contacting an exhaust combustion gas containing sulfur dioxide with an absorbent liquid containing at least magnesium sulfosuccinate and gypsum dihydrate, subjecting the liquid to oxidation with air and to neutralisation with limestone to form a slurry, heating the slurry containing gypsum dihydrate to convert the gypsum dihydrate into α-gypsum, separating the thus formed α-gypsum from the liquid medium by solid-liquid separation, and reusing the resultant separated liquid by recirculation as the absorbent liquid.

The invention includes a method for producing α-gypsum showing a large bulk density and an excellent quality by (a) converting sulfur dioxide contained in exhaust gas into gypsum dihydrate by a process for desulfurisation of exhaust gas and (b) heating the thus formed gypsum dihydrate without separating gypsum dihydrate from the liquid which is to be used for absorbing sulfur dioxide, thereby obtaining α-gypsum. The invention also includes a method for industrially and inexpensively producing α-gypsum by (a') converting sulfur dioxide contained in exhaust gas into α-gypsum and (b') in the same time, while utilising the heat of the exhaust gas, converting gypsum dihydrate which is not derived from the sulfur dioxide in the exhaust gas according to the present desulfurisation method and is obtained by other means, into α-gypsum.

The accompanying drawing is a flow chart for the process for producing α-gypsum is a system for removal of sulfur dioxide from the exhaust combustion gas.

One characteristic feature of the present invention is that a salt of sulfosuccinic acid, preferably magnesium sulfosuccinate as the catalyst for crystallisation is used in the process for producing α-gypsum by heat-dehydrating gypsum dihydrate. A preferred additional characteristic feature is that an exhaust gas containing sulfur dioxide is contacted with an absorbent liquid containing at least magnesium sulfosuccinate and gypsum dihydrate (calcium, sulfate dihydrate), thereby removing sulfur dioxide from the exhaust combustion gas, oxidising the thus formed sulfite by air and then neutralising the thus formed sulfate by limestone, thereby forming gypsum dihydrate (calcium sulfate dihydrate) as a slurry in the absorbent liquid, heating calcium sulfate dihydrate with the absorbent, thereby converting the dihydrate into calcium sulfate hemihydrate (α-gypsum), and carrying out the solid-liquid separation of the aqueous slurry of α-gypsum, the thus separated solid being collected as α-gypsum and the thus separated liquid being used in circulation for contacting with sulfur dioxide in the exhaust gas.

Although the salt of sulfosuccinic acid used in the present invention as the catalyst for crystallisation is not available in the form of an industrial chemical or a chemical reagent, it is easily synthesisable from maleic acid or fumaric acid (refer to Japanese Patent Publication No. 58-25492 (1983). In addition, in the case where the process for producing α-gypsum from gypsum dihydrate is combined with the process for removing sulfur dioxide in an exhaust gas, the salt of sulfosuccinic acid can be synthesized in the process by the use of maleic anhydride while utilising sulfur dioxide in the exhaust gas (refer to DE-OS 3419328).

In addition, as has been described, when sodium salt of lower aliphatic polycarboxylic acid is used as the catalyst for crystallisation, sodium ions coprecipitate with α-gypsum as the form of Na_2SO_4 in the step of conversion of gypsum dihydrate to α-gypsum.

Accordingly, the chemical formula for α-gypsum should correctly be represented as $CaSO_4.nNa_2SO_4.mH_2O$ (where n is form 0 to 1/10 and m is about 1/2). The ratio of the concentration by weight of the coprecipitated sodium ions in α-gypsum to the Na^+ concentration in the liquid medium after the reaction is approximately 1-2.

It has been found that this ratio remains substantially constant over a wide range of the Na+ content in the α-gypsum of 0 to 25,000 mg/kg., even though it may vary somewhat depending on the reaction temperature, the slurry concentration in the reaction system and the composition of the liquid medium,

As is well-known, it is desired that the amount of the sodium ions contaminated into the α-gypsum is as low as possible in view of the physical properties of the α-gypsum during use, and it is required that such an amount is always less than 1200 mg/kg and, preferably, less than 200 mg/kg.

Accordingly, in the case where α-gypsum containing no sodium ions is necessary, it is preferred that magnesium sulfosuccinate is used instead of sodium sulfosuccinate.

When using magnesium sulfosuccinate, since magnesium ions, (in contrast to sodium ions) are not coprecipitated into the α-gypsum, deposited magnesium ions can easily be eliminated by washing the resultant α-gypsum. A salt mixture of the magnesium sulfosuccinate and sodium sulfosuccinate may also be used.

One advantage of sulphosuccinic acid is that it can be as good a catalyst for the crystallisation as succinic acid but at a much lower molal concentration, for instance 1/5th of that required for succinic acid. Another advantage is that whereas both succinic acid and sulphosuccinic acid are excellent catalysts at around neutral pH values succinic acid has low catalytic activity at pH below 4 whilst sulphosuccinic acid gives good activity at pH values of 3 to 4.

It is necessary to use the sulfosuccinate at a concentration of higher than 1 mmol/kg in order to obtain a sufficient catalyst effect for crystallisation thereof.

In general, the conversion reaction is carried out at a temperature of 110 to 150°C.

As can be seen from the process for removing sulfur dioxide from an exhaust gas (desulfurisation process) using an absorbent liquid containing a sulfosuccinate (refer to Japanese Patent Publication No. 58-25492 (1983) and DE-OS 3419328), sulfosuccinate is an excellent absorber for desulfurisation, and a solution containing a sulfosuccinate is an absorbent liquid with an excellent desulfurisation effect in the case where the sulfosuccinate constitutes the main ingredient for the absorption of gaseous sulfur dioxide, as well as in the case where limestone constitutes the main ingredient for the absorption of the sulfur dioxide due to the presence of a small amount of the sulfosuccinate. Carboxylates contained in the absorbent liquid are inevitably decomposed upon air oxidation and the amount of the decomposition depends on the concentration. On the other hand, since the sulfosuccinate is less decomposed as compared with other carboxylates that will act as catalyst for crystallisation (for example, citrate and succinate) and it is effective both for the desulfurisation of the exhaust gas and for conversion to the α-gypsum at a low concentration, the amount of decomposition is remarkably small and the process is very satisfactory from economic point of view.

Although an adipate has been known as a carboxylate that can be used for the desulfurisation of the exhaust gas, it has no catalyst effect for crystallisation, compared to that of the sulfosuccinate, and thus is not suitable for the producation of α-gypsum (Example 1).

In order to combine the desulfurisation process directly with the conversion process for α-gypsum to obtain α-gypsum at a good quality, it is necessary that liquid medium circulating through both of the processes are essentially indentical and can attain the purposes of both of the processes effectively. The sulfosuccinate is a unique component to attain the purposes.

Namely, one of processes according to the present invention comprises a first step of (1) contacting an exhaust gas at high temperature containing gaseous sulfur dioxide with an absorbent liquid containing at least magnesium sulfosuccinate and gypsum dihydrate to capture the sulfur dioxide and (2) subjecting to oxidation with air and to neutralisation with limestone thereby forming gypsum dihydrate in the absorbent liquid, and a second step of (3) converting the thus formed gypsum dihydrate into α-gypsum in the above-mentioned absorbent liquid medium and (4) recovering the thus formed α-gypsum by solid-liquid separation followed by washing, and (5) recycling the separated liquid (filtrate) obtained in the solid-liquid separation and the washing step to the contacting step with the exhaust gas at high temperature as described above.

In wet-type desulfurisation processes, that product gypsum, it is known to humidify and cool the exhaust gas followed by absorption (double-column system), and it is known to directly contact the absorbent liquid with the exhaust gas (single-column type). In the former system, since the exhaust gas is subjected to the desulfurisation process when the water content therein is completely or nearly saturated, it is difficult to maintain the water balance in the desulfurisation step. In the latter system, since the heat possessed in the exhaust gas at high temperature is adiabatically cooled by the absorbent liquid, there is the advantage that water is eliminated by evaporation.

The amount of water evaporated from the absorbent liquid, while varying depending on the temperature and the water content of the exhaust gas, is usually about from 0.7 to 1.1 ton per 10,000 Nm^3 of the exhaust gas. Since about 0.3 ton of water is required as supplemental water that has to be added into the desulfurisation process, such as washing water at the inlet of the high temperature gas and washing water for demister, etc, the amount of water that can actually be eliminately by evaporation is about from 0.4 to 0.8 ton. On the other hand, since about from 1.5 to 2 kg/kg of water is by-product upon converting the gypsum dihydrate into the α-gypsum, water can be eliminated by evaporation in an amount corresponding to the by-product by about 200 to 500 kg per 10,000 Nm^3 of the exhaust gas, when the system of directly contacting with the exhaust gas is employed. In other words, about 200 to 500 kg of the α-gypsum can be produced by subjecting 10,000 Nm^3 of the exhaust gas to desulfurisation treatment. The amount corresponds to from 3,000 to 8,000 ppm as converted to the SO_2 concentration in the exhaust gas.

In the desulphurisation process of the present invention, it is essential that the absorbent liquid to be contacted with the exhaust gas at high temperature contains both the magnesium sulfosuccinate and gypsum dihydrate. The magnesium sulfosuccinate serves both as an absorbent for the sulfur dioxide in the exhaust gas and as a catalyst for crystallisation for converting the gypsum dihydrate into the α-gypsum. The gypsum dihydrate suppresses the generation of scales in the absorbing column.

In the absorbent liquid used herein, it is preferred that the content of the magnesium sulfosuccinate is about from 10 to 100 mmol/kg and the content of the gypsum dihydrate is about from 5 to 25% by weight.

Further, the absorbent liquid may also contain other materials contributing to the absorption of the gaseous sulfur dioxide, for example, limestone. Furthermore, anions as the dissolved ingredient, for example, various organic ions derived from the decomposition of sulfosuccinic acid, SO_4^{2-}, Cl^-, HSO_3^-, etc, as well as cations, mainly Mg^{2+}, a small amount Na^+ and a smaller amount Ca^{2+} may also be present together. Furthermore, a solid component such as calcium sulfite may also be present in addition to the limestone.

For capturing the sulfur dioxide of the exhaust gas using the above-mentioned absorbent liquid and subjecting the thus formed sulfite to oxidation with air and neutralising the thus formed sulfate with limestone (or slaked lime), any method can be used so long as the slurry of the gypsum dihydrate can be obtained finally.

The resultant slurry usually contains the gypsum dihydrate in an amount of from 5 to 25% by weight, has a pH value of from 4 to 8 and at a temperature of from 40 to 80°C. The composition of the slurry corresponds to the composition of the absorbent liquid, from which HSO_3^- as the dissolved ingredient and calcium sulfite and limestone as the solid component are removed.

The gypsum dihydrate slurry obtained by desulfurisation from the exhaust gas is concentrated and subjected to heat treatment. While the quality of the thus obtained α-gypsum is basically determined by the composition of the absorbent liquid, heating temperature and heating time, there is a correlationship between the temperature and the reaction item and in the case of using the absorbent as the medium, the reaction may be carried out under the conditions within the temperature of 110 to 150°C, preferably 110 to 140°C and reaction time of 1 to 3 hours considering the heat energy consumption and the cost of the appartus. Explanation will then be made to the composition for the absorbent liquid together with the effects caused by the direct combination with the desulfurisation process as below.

At first, the absorbent liquid contains sulfosuccinic acid as the anions and the appropriate concentration thereof is from 10 to 100 mmol/kg while defining the desulfurisation process. The catalyst effect for crystallisation of sulfosuccinc acid shows no significant difference within the above-specified range of concentration, where the α-gypsum of a sufficiently high bulk density can be obtained (see Example 2).

Since sulfosuccinc acid is decomposed through induced oxidisation in the desulfurisation process, organic anions as the decomposing by-product thereof are contained a little and the presence thereof has no substantial effect on the bulk density.

SO_4^{2-} is present in the liquid mainly due to the dissolution of Mg in the limestone. Although the concentration of the dissolved Ca^{2+} is reduced as the SO_4^{2-} concentration increases to reduce scaling in the desulfurisation process, an excess concentration reduces the rate of oxidation of the sulfite.

Accordingly, the concentration of SO_4^{2-} may vary greatly depending on the design of the desulfurisation process and it is usually within a range from about 0.5 to about 8% by weight. When using such a liquid as a medium for the α-gypsum conversion, the temperature in the conversion process is lowered as the SO_4^{2-} concentration increases to provide an advantage in view of the heat energy. However, the upper limit thereof is generally 8 - 10% by weight since an excessively high concentration tends to produce anhydrous gypsum. Accordingly, α-gypsum at a sufficiently high bulk density can be obtained within a range of the SO_4^{2-} concentration usually employed in the desulfurisation process.

Cl^- derived from chlorides in the water used and from HCl gas contained in the exhaust gas is present in the concentrated form in the absorbent liquid. The Cl^- concentration in the absorbent liquid is associated with the corrosion of metals in the desulfurisation plant and it is usually controlled to less than 1 - 2% by weight.

While no practical problems arise for the conversion into α-gypsum, in the case of the above-mentioned concentration, since an excessively high concentration tends to produce anhydrous gypsum in the same manner as in SO_4^{2-} concentration, the upper limit is defined as 6 - 8% by weight. Accordingly, the composition of the liquid medium for the production of the α-gypsum has no contradiction with the liquid composition for the desulfurisation process.

Referring then to cations as the composition of the liquid, the cations used in the absorbent liquid for desulfurisation are usually Mg^{2+} and Na^+ and, in addition, a small amount of Ca^{2+} corresponding to the dissolving amount of gypsum. While characteristic process constitutions are taken for the desulfurisation process while utilising the difference in the properties of the respective ions, liquid containing only Mg^{2+} or mainly Mg^{2+} and a low amount of Na^+ have often been used in the recent desulfurisation process using limestone as the neutralising agent. On the other hand, it is highly preferred that the liquid madium for the α-gypsum conversion contains only Mg^{2+}, by which α-gypsum with no coprecipitation of Na^+ and having high bulk density can be obtained (see Example 5).

A specific embodiment for practicing the present invention will now be explained referring to the appended drawing.

In the drawing, a desulfurisation facility that produces gypsum dihydrate as a by-product is denoted by a reference numberal 1, in which exhaust gas 2 containing gaseous sulfur dioxide is desulfurised into a cleaned gas 3 using an absorbent liquid containing at least magnesium sulfosuccinate and gypsum dihydrate, and limestone or slaked lime as a neutralising agent 4 and an oxidising air 5 are supplied to the absorbent liquid to form the slurry of gypsum dihydrate. The resultant gypsum dihydrate slurry 6 is recovered and concentrated in a thickener 7. The concentrated gypsum dihydrate slurry 9 is served for the production of α-gypsum, while an overflow liquid 8 is returned to the desulfurisation facility 1. This concentration of the slurry is carried out for decreasing the amount of the processing liquid per unit weight of the α-gypsum as well as for decreasing the volume of the device in the succeeding stage and saving the heat energy required for heating. Accordingly, it is desired that the concentration of the thickened slurry 9 is as high as possible to a limit that the slurry can be handled and it is preferably from 30 to 60% by weight of concentration.

The gypsum dihydrate slurry 9 to be used for the production of the α-gypsum is supplied under pressure by a pump 10 to a reaction vessel 11 for conversion into α-gypsum. Since it is required to heat the slurry to 110 - 104°C (at 0.5 - 2.7 kg/cm²G pressure) for the convertion reaction to α-gypsum, the temperature is elevated by a heat exchanger 12 and a steam heater 13. The heating may also be conducted by blowing steam directly into the reaction vessel 11 instead of using these indirect heat exchangers 12, 13. The reaction vessel 11 for the α-gypsum conversion may either be a multiple-vessel flow system as shown in the drawing or a batchwise switching type.

As described above, while the α-gypsum conversion reaction is completed within 1 - 3 hours at a predetermined temperature in the reaction vessel 11, if a small amount of seed crystals 14 of the α-gypsum is added previously, the reaction rate in the α-gypsum conversion can effectively be increased.

The resultant α-gypsum slurry is supplied to a separator 16 after being cooled to an atomospheric boiling point and lowered to ambient pressure. In this case, cooling can be attained either by way of an indirect cooling method or using flash evaporation. Steam obtained through the flash evaporation can be utilised for heating the gypsum dihydrate slurry as described above.

α-Gypsum cakes obtained through the solid-liquid separation in the separator 16 are washed with hotwater. In this case, in order to avoid the reconversion of the α-gypsum to the gypsum dihydrate, the slurry and the α-gypsum cakes are kept at a temperature above 84°C and deposited water content is rapidly removed in a drier 17 to obtain α-gypsum 18. The filtrate and the washing liquid 19 from the separator 16 are returned to the desulfurisation facility 1, so that the washing liquid used for the α-gypsum also serves as a supplementary water to the desulfurisation system.

Upon converting the gypsum dihydrate produced in the absorbent liquid into the α-gypsum as described above, magnesium sulfosuccinate contained in the absorbent liquid is used as the catalyst for crystallisation in the present invention. By using the absorbent liquid as the liquid medium and adding the above-mentioned gypsum dihydrate and other gypsum dihydrate produced by means other than the desulfurisation system (hereinafter referred to as "other gypsum dihydrate") as required to the absorbent liquid, the other gypsum dihydrate can also be converted into the α-gypsum. While there is no particular restriction to the place where the other gypsum dihydrate is added to the absorbent liquid for the conversion into the α-gypsum, it may actually be added at (i) the step of adding limestone for neutralisation to the absorbent liquid having captured the gaseous sulfur dioxide absorption step (step A in the drawing), at (ii) the step where the gypsum dihydrate slurry produced in the absorbent liquid as described above is branched from the desulfurisation step and converted into the α-gypsum (step B in the drawing), or to (iii) the liquid medium obtained after the conversion of the gypsum dihydrate in the slurry into the α-gypsum using the absorbent liquid containing magnesium sulfosuccinate as the medium and then separating the resultant α-gypsum (step C in the drawing).

In the specification, the other gypsum dihydrate means those gypsum dihydrates other than the gypsum dihydrats derived from the gaseous sulfur dioxide contained in the exhaust gas that is being treated. They include gypsum produced from a previous desulfurisation process, as well as chemical gypsum such as ammonium sulfate gypsum, natural gypsum and, in addition, phosphoric acid gypsum and gypsum produced by subjecting fluoric acid anhydrous gypsum to hydration.

The place where the other gypsum dihydrate is added can be selected properly depending on the quality of the gypsum dihydrate used and the quality of the objective α-gypsum. For instance, since the gypsum dihydrate formed by the absorption of the gaseous sulfur dioxide in the high temperature exhaust gas usually contains a small amount of soot derived from the exhaust gas, if the other gypsum dihydrate is added at the step of adding limestone to the absorbent liquid or at the step of converting the gypsum dihydrate slurry formed in the absorbent liquid into the α-gypsum (A or B in the drawing), the entire α-gypsum obtained by converting these gypsum dihydrates contains a low amount of soot. The above mentioned method of adding the other gypsum dihydrate can be employed in the case of producing α-gypsum suitable for the manufacture of, for example, boards in which high quality is not required.

The gypsum dihydrate formed in the liquid containing magnesium sulfosuccinate is obtainable as crystals with a preferably small aspect ratio as the starting material for the α-gypsum, and the other gypsum dihydrate can also be grown to those crystals with a small aspect ratio by holding them for a long period of time in the liquid containing magnesium sulfosuccinate. Accordingly, in the case where the other gypsum dihydrate added from out of the system is in the form of crystals with a large aspect ratio, it is preferred to add the other gypsum dihydrate so as to be circulated to the desulfurisation step (step A in the drawing) so that it is held for long periods of time in the absorbent liquid containing magnesium sulfosuccinate.

Furthermore, if it is intended to produce a great amount of α-gypsum at high purity, the other gypsum dihydrate obtained out of the system is preferably added to the purified overlow liquid from the thickener that is obtained upon thickening the gypsum dihydrated slurry (step D in the drawing), or to the separated mother liquid after the formation of the α-gypsum further followed by washing (step C in the drawing), to convert into the α-gypsum.

In the present invention, by-product water resulting from convertion of the gypsum dihydrate into α-gypsum is returned to the desulfurisation step to contact with the exhaust combustion gas at high temperature in any of the above mentioned cases, so that water in an amount corresponding to the by-product water is eliminated by evaporation due to the heat from the exhaust gas, simultaneously with the absorption of the gaseous sulfur dioxide.

In the present specification the concentration is indicated for the solid component based on the total slurry and for the dissolved component based on the aqueous solution excluding the solid component.

The present invention will now be described specifically together with the effects thereof, in the examples shown below.

Example 1

This example shows a case where α-gypsum was produced by using sulfosuccinates (the present invention) as the catalyst for crystallisation and known catalysts (comparative example) at various concentrations.

As a producing apparatus, an autoclave of 2.5 litre inner volume equipped with a stirrer was used. The inside temperature of the autoclave was adapted to be controlled to a specified temperature by an externally heating type electric heater.

To the autoclave as described above, 375 g of gypsum dihydrate drived from desulfurisation process and washed with water and dried (Sample-1 in Example 8 described later) and 1.5 kg of various kinds catalyst for crystallisation prepared into hemihydrating medium at the concentration shown in Table 1 were charged respectively (at slurry concentration of 20% by weight). The slurry was subjected to heat treatment at a temperature of 128°C ± 1°C for 1.5 hours.

The slurry after the heat treatment was filtrated while hot at 95°C, and the resultant solid crystals were washed with 320 g of hot water at 95°C and then directly dried at 100°C.

The thus obtained crystals were judged whether they were converted into the α-gypsum or not by the measurement for the water of crystallisation, and by applying differential thermal analysis and X-ray diffraction method.

The results are shown in Table 1 together with the kind of the crystallisers and the concentration thereof in the liquid medium.

TABLE 1

Experiment No.		Modium composition		Properties of the formed crystals			
		Catalyst for crystallization	Concentration (mmol/kg)	Water of crystallization (wt%)	Bulk$^{1)}$ density (g/cm^3)	Aspect ratio	Length (μ)
The present invention	11	Trisodium sulfosuccinate	2.0	6.3	1.48	1 - 2	20-100
	12	″	12.3	5.9	1.62	1	20-100
Comparative Example	13	Disodium succinate	2.0	5.9	1.34	2 - 5	20-100
	14	″	12.3	6.0	1.46	1 - 5	20-100
	15	″	61.7	6.0	1.61	1	50-150
	16	Trisodium citrate	2.0	17.1	-	-	-
	17	″	12.3	19.1	-	-	-
	18	Disodium adipate	61.7	5.9	0.46	10-30	Several tens - hundred & several tens
	19	Only water	0	6.2	0.19	several tens	″

(Note) 1) is bulk density of the product after tapping

The crystals obtained in Experiment Nos. 11-15 and 18, 19 in the table were judged to be α-gypsum.

As can be seen from Table 1, as the concentration of the catalyst for crystallisation in the liquid medium increases, the bulk density of the α-gypsum increases accordingly, the catalyst effect for crystallisation becomes increased. Further, comparing the concentration of the catalyst for crystallisation required for obtaining α-gypsum of an identical bulk density, it can be recognised that the molal concentration of the sulfosuccinate used in the present invention can be reduced to about 1/5 of that of the conventional succinate, and the sulfosuccinate has an excellent catalyst effect for crystallisation.

The dehydrating reaction did not proceed so far in the crystals obtained in Experiment Nos. 16 and 17 and it can be said that heat treatment at a higher temperature is required in the case of using citrate as the catalyst for crystallisation. By the way, it is described that a temperature of from 140 - 150°C is required also in Japanese Patent Publication No. 57-25495 (1982).

Since the α-gypsum can be obtained by using the sulfosuccinate as the catalyst for crystallisation at a lower temperature than that where the citrate is used, the present invention is advantageous also in view of the production cost.

While adipic acid may be proposed as an organic carboxylic acid that can be used for the desulfurisation process, it is inferior to sulfosuccinc acid in its catalyst performance.

Example 2

In the present example, the effect of the concentration of the sulfosuccinate under the coexistence of an inorganic magnesium salt was examined.

The same procedures as described in Example 1 were carried out using the slurry of the following composition, except for setting the reaction temperature to 118°C ± 1°C and the reaction time to 1.5 hour, to obtain the results as shown in Table 2.

Hemihydrating medium	1.5kg
Trisodium sulfosuccinate	variable
$MgSO_4$ (converted as SO_4^{2-})	5 wt%
$MgCl_2$ (converted as Cl^-)	1 wt%
pH	6.0
Gypsum dihydrated from desulfurisation	375 g

TABLE 2

Experiment No.	*Trisodium sulfosuccinate*	*Bulk[1] density g/cm^3*	*Aspect ratio*	*Length*
21	61.7 mmol/kg	1.70	1 - 2	20-100
22	12.3	1.64	1 - 3	30-100
23	0	0.33	about 20	50-200

(note) 1): Refer to Table 1

All of the resultant crylstals were α-gypsum.

It can be seen that the sulfosuccinic acid has a sufficient catalytic performance at a considerably lower concentration and further that α-gypsum at high quality can be obtained from the liquid containing SO_4^{2-} and Cl^- as anions in addition to sulfosuccinic acid. In addition, it can also be recognised that only α-gypsum at low bulk density can be obtained merely by the use of the inorganic magnesium.

Example 3

The present examples shows the mode where the reaction temperature can be decreased by coexisting an inorganic salt to the sulfosuccinate as the catalyst for crystallisation and the effect of the pH at the reaction. The result in the case of using the succinate is also shown together as a comparison. The same procedures as in Example 2 were carried out using the slurry of the following composition, to obtain the result as shown in Table 3.

Hemihydrating medium	1.5 kg
Trisodium sulfosuccinate	61.7 mmol/kg
$MgSO_4$ (converted as SO_4^{2-})	5 wt%
$MgCl_2$ (converted as Cl^-)	1 wt%
Gypsum dihydrated from desulfurisation	375 g

In the Comparative Example, disodium succinate was used in the an equi-molar amount instead of trisodium sulfosuccinate as described above.

TABLE 3

		Medium composition		Physical property of formed crystals		
Experiment No.		*Catalyst for crystallization*	*pH*	*Bulk[1] density (g/cm^3)*	*Aspect ratio*	*Length (μ)*
The present invention	31 (21)	Trisodium sulfosuccinate	6.0	1.70	1 - 2	20 - 100
	32	"	3.7	1.52	3 - 5	50 - 120
Comparative Example	33	Disodium succinate	3.7	0.81	7 - 13	50 - 200

(Note) 1): Refer to Table 1.

It can be seen that while all of the resultant crystals are α-gypsum, the reaction temperature can be reduced by 10°C as compared with Example 1 by coexisting the inorganic salt in the liquid medium.

In addition, while there is a little effect on the catalyst effect for crystallisation if the pH of the liquid medium is reduced in the case of using the sulfosuccinate (pH was adjusted by the addition of H_2SO_4), when using succinate catalyst effect for crystallisation is significantly reduced upon pH reduction It has been known that when using an organic carboxylic acid type catalyst the catalyst effect for crystallisation is reduced with reduction the pH value of the liquid medium.

As described above, since the effect of pH can substantially be excluded when the sulfosuccinate is used as the catalyst for crystallisation, intrusion of heavy metals which may possibly be incorporated in the gypsum dihydrate as the starting material into the α-gypsum can be prevented and accordingly, α-gypsum at high purity can be obtained advantageously.

Example 4

The present example shows the relationship between the concentration of the gypsum dihydrate slurry and the conversion into the α-gypsum.

The procedures as in Example 1 were carried out using the hemihydrating liquid medium as below except for setting the reaction temperature to 122 ± 1°C, the reaction time to 1.5 hours and using the washing water in the amount of 570 g, 850 g and 1300 g respectively, to obtain the results shown in Table 4-1.

Liquid medium 1 kg	
Trisodium sulfosuccinate	30 mmol/kg
$MgSO_4$ (converted as SO_4^{2-})	2.5 wt%
$MgCl_2$ (converted as Cl^-)	0.5 wt%
pH = 6.0	

TABLE 4-1

Experiment No.	*Gypsum dihydrate amount (slurry concentration)*	*Bulk[1] density (g/cm³)*	*Aspect ratio*	*Length (μ)*
41	0.667 kg (40 wt%)	1.67	1 - 3	30 - 100
42	1.0 kg (50 wt%)	1.56	1 - 3	30 - 100
43	1.5 kg (60 wt%)	1.55	1 - 3	30 - 100

(Note) 1): Refer to Table 1.

All of the resultant crystals were α-gypsum. While the bulk density is lowered as the slurry concentration is higher, the effect is low. The slurry at such high concentration can be handled as a fluid, because the bulk densities both for the starting gypsum dihydrate and α-gypsum procuts was pulverised in ball mill for 30 min and the bulk density, mixing-water amount for normal consistency and compression strength were measured respectively for the pulverisates, to obtain the results as shown in Table 4-2.

TABLE 4-2

Experiment No.	*Bulk[1] density (g/cm³)*	*Mixing-water amount for normal consistency (%)*	*Dry compression strength (kg/cm²)*
41	1.80	30	430
42	1.77	32	400
43	1.77	33	390

(Note) 1): Refer to Table 1.

Each of the α-gypsum has satisfactory physical properties as shown in the Table.

Example 5

The present example shows the kind and the concentration of cations. The same procedures as in Example 2 were carried out using the slurry composition as below, to obtain the results as shown in Table 5.

Hemihydrating liquid medium	1.5 kg
(anion concentration	1.508 equivalent/kg)
Sulfosuccinate acid	61.7 mmol/kg
SO_4^{2-}	5 wt%
Cl^-	1 wt%
pH=6.0	
Gypsum dihydrate from desulfurisation	375 g

TABLE 5

Experiment No.	*Cation equivalent of hemihydrating liquid medium*		*Bulk density[1] (g/cm³)*	*Aspect ratio*	*Length (μ)*
	Mg^{2+} (%)	Na^+(%)			
51 (21)	87.7	12.3	1.70	1 - 2	20 - 100
52	78.5	21.5	1.53	2 - 3	50 - 100
53	69.2	30.8	1.51	3 - 5	30 - 100
54	59.9	40.1	1.30	4 - 7	50 - 120

(Note) 1): Refer to Table 1.

All of the resultant crylstals were α-gypsum. It can be seen from the result that α-gypsum at higher bulk density can be obtained as the amount of Na^+ decreases.

Example 6

The present example shows the relationship between the Na^+ concentration in the liquid medium and the coprecipitation of Na^+ into α-gypsum in the case where sodium solfocuccinate, magnesium sulfosuccinate and a mixed solution thereof are used as the catalyst for crystallisation.

The reaction was carried out by the same procedures as described in Example 1 using a 60 wt% slurry with the composition as stated below except for effecting the reaction at a temperature of 130 ± 1°C for 20 minutes and at a temperature of 125 ± 1°C for 40 minutes respectively and washing with 1.3 kg of hot water after the reaction, to obtain the results shown in Table 6.

Hemihydrating liquid medium	1.0 kg
Sodium sulfosuccinate and/or Magnesium sulfosuccinate	31 mmol/kg
$MgSO_4$ (converted as SO_4^{2-})	2.5 wt%
$MgCl_2$ (converted as Cl^-)	0.5 wt%
pH	6 - 6.5
Gypsum dihydrate from desulfurisation	1.5 kg

TABLE 6

Experiment No.	Na^+ concentration in medium (mg/kg)	Reaction temperature and time	α-gypsum Bulk[1] density (g/cm^2)	Na^+ content (mg/kg)	Na^+ concentration in the medium after reaction (mg/kg)	Na^+ concentration ratio
61	2140	130±1°C 20 min	1.50	1100	620	1.8
62	1605	"	1.49	820	430	1.9
63	1070	"	1.47	570	290	2.0
64	535	"	1.47	300	140	2.1
65	0	"	1.52	0	0	-
66	1070	125±1°C 40 min	1.56	570	310	1.8
67	535	"	1.42	270	155	1.7

(Note) 1): Refer to Table 1.

Notes:

(1) Sodium sulfosuccinate and magnesium sulfosuccinate are used as the catalyst for crystallisation in Experiment Nos. 61 and 65 respectively, sodium sulfosuccinate and magnesium sulfosuccinate mixed in the molar ratios of 3 : 1, 2 : 2, 1 : 3, 2 : 2 and 1 : 3 are used in Experiment Nos. 62, 63, 64, 66 and 67 respectively.

(2) The ratio for the Na^+ concentration indicates the ratio between the Na^+ content in the α-gypsum and the Na^+ concentration in the liquid medium after the reaction, which is approximately 2.

As can be seen from Table 6, since the amount of the copreciptation of Na^+ into the α-gypsum is increased as the Na^+ concentration in the liquid medium goes higher, it is required tp reduce the Na^+ concentration in the liquid medium by using sulfosuccinic acid, for example, in the form of magnesium salt in the case where the reduction in the Na^+ content in the α-gypsum is required.

Example 7

Absorption of SO_2 in an exhaust combustion gas at high temperature

Exhaust combustion gas from C-heavy oil (temperature 180°C, SO_2 concentration 1400 ppm) was brought into a direct contact at the rate of 30,000 Nm^3/hr with a absorbent liquid containing 45 mmol/kg of magnesium sulfosuccinate and from 10 to 15% by weight of crystalline gypsum dihydrate, thereby causing the gaseous sulfur dioxide in the exhaust gas to be absorbed and evaporating a portion of the water content in the absorbent liquid by the heat of the exhaust gas. Water was evaporated at the rate of 3.1 ton/hr accompanying the effluent gas (temperature 58°C, SO_2 concentration 1 -2 ppm, humidity 18 v%) purified by the absorption and discharged.

Formation of gypsum dihydrate from gaseous sulfur dioxide

The absorbent liquid after the absorption was subjected to neutralisation with limestone (200 mesh powder) and to oxidation with air in the conventional manner to form a gypsum dihydrate slurry at a concentration of from 10 to 15% by weight and regenerate the absorbent liquid. Then, a portion of the slurry is branched and gypsum dihydrate cake (330 kg/hr on dry base) was obtained through centrifuge.

The composition of the liquid component in the gypsum dihydrate slurry was as follows:

Sulfosuccinic acid	45 mmol/kg
SO_4^{2-}	4.6 wt%
Cl^-	0.8 wt%
Mg^{2+}	13040 mg/kg
Na^+	4050 mg/kg
pH	5.8

In the operation of the apparatus for the treatment with the absorption and formation of the gypsum dihydrate, 1.2 ton/hr of water was used for the washing of the exhaust gas introducing wall in the absorption column, pump sealing or the like and, further, 2.0 ton/hr of water was supplemented as the balance water.

Conversion of gypsum dihydrate to α-gypsum (Experiment No. 71)

12.5 wt% gypsum dihydrate slurry obtained from a portion of the gypsum dihydrate slurry formed as described above was held to obtain a 30 wt% slurry, 2.5 kg of which (containing 0.75 kg of gypsum dihydrate) were changed in an autoclave of 2.5 liter inner volume equipped with a stirrer and subjected to heat treatment at a solution temperature of 115°C ± 1°C for 2.5 hours under stirring. The slurry was filtered while hot at 95°C and, after washing with hot water at 95°C, the crystals were directly at 100°C.

The resultant crystals contained 6.1% by weight of water of crystallisation and confirmed to be α-gypsum by differential thermal analysis and X-ray diffraction. The crystals were shaped with an aspect ratio of from 1 to 3 and a length of about from 30 to 110 μm and and a bulk density of 1.61 g/cm³

Then, when the α-gypsum thus obtained was pulverised in a ball mill for 30 min, the bulk density was increased to 1.70 g/cm³. The pulverisate contained a mixing-water amount of normal consistency of 37% and had a dry compression strength of 320 kg/cm³/

Conversion of gypsum dihydrate into α-gypsum (Experiment No.72

To a 12.5 wt% gypsum dihydrate slurry obtained from a portion of the gypsum dihydrate slurry (2kg) formed as described above (containing 0.25 kg of gypsum dihydrate), were added 0.5 of gypsum dihydrate obtained out of the system (board grade gypsum dihydrate obtained from exhaust gas sulfurising process by the sodium sulfite gypsum method) to form a 30 wt% slurry.

The slurry was charged in an autoclave of 2.5 liter inner volume equipped with a stirrer and subjected to heat treatment at a solution temperature of 115°C ± 1°C for 2.5 hours under stirring. The slurry thus obtained was filtered while hot at 95°C and, after washing with 0.9 gk of hot water at 95°C, the crystals were directly dried at 100°C.

The amount of the washing water was determined such that magnesium sulfosuccinate deposited to remain on the crystals was reduced to less than 100ppm. The amount of water required for the washing corresponds to 1.2 ton/hr even in a case of obtaining the α-gypsum in an amount three times as large as the gypsum dihydrate obtained from the gaseous sulfur dioxide in the exhaust gas, which is less than 2.0 t/hr of water supplied as the balance water. Accordingly, it can be understood that α-gypsum can be obtained in an amount greater than of α-gypsum obtained form the gypsum dihydrate derived from the gaseous sulfur dioxide in the exhaust gas.

The crystals obtained as described above contained 6.1% by weight of water of crystallisation and were confirmed to be α-gypsum by differential thermal analysis and X-ray diffraction. The crystals were shaped with a aspect ratio of from 2 to 5 and the length of from 30 to 110 μm and had a bulk density of 1.21 g/cm³.

When the α-gypsum was pulverised in a ball mill for 30 minutes, the bulk density was increased to 1.60 g/cm³ and the pulverisate contained a mixing-water amount for normal consistency of 38% and a dry compression strength of 310 kg/cm².

Example 8

The present example shows the result of the conversion into α-gypsum on various gypsum dihydrates which are added externally to the system and served for the conversion into α-gypsum by using a hemihydrating liquid medium containing magnesium sulfosuccinate as the catalyst for crystallisation.

The kind and the property of the gypsum dihydrates used for the experiment are as shown in Table 7. The gypsum dihydrates were dried before use for the experiment.

TABLE 7

Sample No.	*Gypsum dihydrate*	*Water content (wt%)*	*Bulk density of the product after washing, drying and then tapping (g/cm³)*	*Water of crystalization (wt%)*
1	Produced from the desulfurization step in Example 7	5	1.43	20.4
2	Board grade product obtained from the desulfurization process by the sodium sulfite gypsum method	7	1.09	20.6
3	Phosphoric acid gypsum obtained from hemihydrate-dihydrate method	10	1.17	19.3
4	Produced from hydrofluoric acid by-product anhydrous gypsum through hydration	10	0.85	16.9
5	Active silicic acid by-produced gypsum	4	1.24	20.8
6	Produced from refining desulfurization	7	1.06	20.9

The composition of the hemihydrating liquid medium used for the conversion of the gypsum dihydrate into he α-gypsum is as follows. Composition of the hemihydrating liquid medium (per 1 kg)

Magnesium sulfosuccinate	6.94 g (30 mmol)
$MgSO_4$	31.35 g (2.5 wt% as SO_4^{2-})
$MgCl_2$	4.52 g (0.5 wt% as Cl^-)
NaCl	2.63 g
pH	6.0

Conversion into α-gypsum in each of the examples was carried out under the conditions as specified below.

Experiments 81 and 82

To an autoclave with inner volume of 2.5 liter equipped with a stirrer, were charged 1.5 kg of gypsum sample and 1.0 kg of the liquid medium as described above, which were subjected to heat treatment at a solution temperature of 122 ± 1°C for 1.5 hours under stirring. The resultant slurry was filtered while hot at 95°C and, after washing with 1.3 kg of hot water at 95°C, the crystals were directly dried at 100°C.

Experiments 83 and 84

The same procedures as in Experiment 81 were carried out except for using 1 kg of the gypsum sample.

Experiment 85 and 86

The same procedures as in Experiment 81 were carried out except for the reaction temperature to 125°C ± 1°C and the reaction time to one hour. The results for each of the experiments are as shown in Tables 8-1 through 8-3.

TABLE 8-1

Experiment No.		*81*	*82*
Tested gypsum dihydrate		*Sample 1 (1.5 kg)*	*Sample 1 (0.5 kg)* *Sample 2 (1.0 kg)*
Property of α-gypsum	Water of crystallization (wt%)	6.06	6.10
	Bulk density¹⁾(g/cm³)	1.55	1.30
	Aspect ratio	1 - 3	1 - 3
	length (μ)	30 - 100	30 - 100
	Apparent density of ball mill-pulverizate (g/cm³)	1.77	1.69
	Mixing-water amount for normal consistency (%)	33	34
	Dry compression strength (kg/cm²)	390	380

(Note) 1): Refer to Table 1.

Note: While the properties of the α-gypsum obtained from the mixed sample in Experiment No. 82 are somewhat inferior as compared with those in Experiment No. 81, they can still be estimated as an α-gypsum of good quality.

TABLE 8-2

Experiment No.		*83*	*84*
tested gypsum dihydrate		*Sample 1 (333 g)* *Sample 3 (667 g)*	*Sample 1 (333 g)* *Sample 4 (667 g)*
Property of α-gypsum	Water of crystallization (wt%)	6.20	5.19
	Bulk density¹⁾(g/cm³)	0.91	1.59
	Aspect ratio	1 - 3	1 - 3
	Length (μ)	2 - 30	2 - 20

(Note) 1): Refer to Table 1.

Note: α-gypsum in Experiment No. 83 had a low bulk density and α-gypsum in Experiment No. 84 was incorporated with anhydrous gypsum and both of them are restricted in the application use in view of their quality.

TABLE 8-3

Experiment No.		*85*	*86*
	Tested gypsum dihydrate	sample 5 (1.5 kg)	sample 6 (1.5 kg)
	Water of crystallization (wt%)	5.83	5.81
	Bulk density (g/cm^3)	1.44	1.40
	Aspect ratio	1-5	1-3
Property of α-gypsum	Length (μ)	30-100	20-50
	Mixing-water amount for normal consistency (%)	37.6	38.5
	Whiteness (HB%)	92.9	91.0
	Coagulating time initial starting final starting	 6 min 15 sec 29 min	 7 min 45 sec 36 min
	Expansion coefficient of coagulate (three hours after) (%)	0.727	0.642
	Wet tensile strength (three hours after, kg/cm^2)	19.1	19.8
	Wet compression strength (three hours after, kg/cm^2)	138	126

Note: As can be seen from the table, both of the α-gypsum obtained from the Samples 5 and 6 can be estimated as standard α-gypsum at high purity.

CLAIMS

1. A method in which α-form gypsum hemihydrate is made by conversion of gypsum dihydrate comprising heating an aqueous slurry containing gypsum dihydrate and a salt of sulfosuccinic acid as a catalyst for crystallisation.

2. A method according to claim 1, wherein the concentration of the salt of sulfosuccinic acid is 1 to 100 mmol/kg based on the aqueous solution.

3. A method according to claim 1, wherein the salt of sulfosuccinic acid is magnesium sulfosuccinate.

4. A method for producing α-form gypsum hemihydrate, comprising contacting an exhaust combustion gas containing sulfur dioxide with an absorbent liquid containing at least magnesium sulfosuccinate and gypsum dihydrate, subjecting the product to oxidation with air and to neutralisation with limestone, heating the thus formed slurry containing gypsum dihydrate to convert the gypsum dihydrate into α-form gypsum dihydrate, separating the thus formed α-form gypsum hemihydrate from a liquid medium by solid-liquid separation, and reusing the thus obtained, separated liquid by recirculation as the absorbent liquid.

5. A method according to claim 4, wherein the conversion of gypsum dihydrate into α-gypsum hemihydrate is carried out by heating an aqueous slurry containing gypsum dihydrate obtained in the the method, magnesium sulfosuccinate and gypsum dihydrate produced by a different method.

6. A method according to claim 4, wherein the conversion of gypsum dihydrate into α-gypsum hemihydrate is carried out by heating an aqueous slurry comprising gypsum dihydrate produced by a different method and a filtrate that is a liquid medium obtained by heating an absorbent liquid containing gypsum dihydrate and magnesium sulfosuccinate, and separating the thus formed α-form gypsum hemihydrate.

7. A method according to claim 6, wherein the liquid medium is a separated supernatant liquid obtained by concentrating an aqueous slurry contained gypsum dihydrate produced by the method for removing sulfur dioxide from the exhaust combustion gas.

8. A method according to claim 5 or claim 6, wherein the gypsum dihydrate produced by a different method is selected from gypsum produced by another method for removing sulfur dioxide from the ex-

haust combustion gas, chemical gypsum, natural gypsum, phosphoric-acid gypsum and gypsum produced by subjecting fluoric acids anhydrous gypsum to hydration.

9. A method according to claim 4, wherein the concentration of the salt of sulfosuccinic acid is 10 to 100 mmol/kg based on the absorbent liquid and the concentration of gypsum dihydrate is 5 to 25% by weight based on the absorbent liquid.

10. A method according to claim 4, wherein the concentration of gypsum dihydrate when converting gypsum dihydrate into α-gypsum hemihydrate, is 30 to 60% by weight based on the aqueous slurry.

11. A method according to claim 1 or 4, wherein the conversion is carried out at a temperature in the range of 110 to 150°C.

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