## DESCRIPTION

TITLE OF INVENTION: METHOD FOR PRODUCING CALCIUM CARBONATE

### Technical Field

[0001]

The present invention relates to a method for producing calcium carbonate.

### Background Art

[0002]

In recent years, efforts have been made to "carbon recycling" for suppressing $CO_2$ emissions by recovering and effectively utilizing $CO_2$ (carbon dioxide) as resources in order to realize carbon neutrality.

The applicant of the present application proposes a hydraulic composition containing a predetermined amount of calcium carbonate as disclosed in Patent Document 1. According to the hydraulic composition, it is possible not only to reduce a discharged amount of $CO_2$ by reducing a used amount of cement while maintaining material properties such as strength, but also to fix $CO_2$ inside concrete as calcium carbonate.

[0003]

Various techniques have been proposed so far with respect to the method for producing calcium carbonate used in Patent Document 1.

For example, Patent Document 2 proposes a method for mixing one or both of an aqueous dispersion of calcium hydroxide and an aqueous dispersion of partially carbonated calcium hydroxide with seed crystals, and then blowing carbon dioxide or a carbon dioxide-

containing gas into the obtained aqueous dispersion to be carbonated, thereby producing precipitated calcium carbonate. Herein, the mixing is performed by shear stirring at a stirring circumferential speed of 7m / s or more.

Further, Patent Document 3 proposes a method for adding an alkali agent to waste seawater after magnesium hydroxide is produced from seawater, adjusting a pH of the waste seawater to more than 11 and 13 or less, and causing a gas containing carbon dioxide to react with a calcium component of the waste seawater for a time set in advance so as to be longer as the pH of the waste seawater to which the alkali agent has been added is higher.

## Prior Art Document

### Patent Document

[0004]

Patent Document 1: International Publication No. WO2021 /256484

Patent Document 2: Japanese Patent Unexamined Application No. H11-11941

Patent Document 3: Japanese Patent No.7138256

## SUMMARY OF INVENTION

### PROBLEMS TO BE SOLVED BY INVENTION

[0005]

The methods for producing calcium carbonate of Patent Documents 2 and 3 are both methods for blowing a gas containing carbon dioxide into a liquid containing calcium ion (so-called liquid phase methods).

Therefore, the methods for producing calcium carbonate of Patent Documents 2 and 3 require a large amount of water for dispersing raw materials, and may require a preliminary treatment for the raw materials (the shearing and stirring treatment of Patent Document 2) or pH control in a liquid phase (the adjustment treatment of Patent Document 3).

Accordingly, the present inventors conceived to propose a completely novel method for producing calcium carbonate, which is different from the liquid phase methods of Patent Documents 2 and 3. However, the present inventors considered that, when the production efficiency of calcium carbonate ((i.e., balance between the amount of calcium carbonate produced within a predetermined time (absorption yield of carbon dioxide) and the energy required for production such as operation of an apparatus and equipment (i.e., emission amount of carbon dioxide)) is not excellent, even if a new method for producing calcium carbonate is proposed, it is not adopted in practice.

[0006]

In view of the above, an object of the present invention is to provide a novel method for producing calcium carbonate excellent in production efficiency.

## MEANS FOR SOLVING THE PROBLEMS

[0007]

The above problems can be solved by the following means.

A method for producing calcium carbonate according to the present invention includes a preparation step of preparing a raw material containing calcium hydroxide and having a water content of 0.3 to 40%, and a reaction step of supplying a gas containing carbon dioxide to the raw material while stirring the raw material and maintaining the water content of the raw material at 0.3 to

40%, to cause the calcium hydroxide to react with the carbon dioxide.

According to the present invention, in the preparation step and the reaction step, the water content of the raw material is controlled to be within a predetermined range, so that calcium hydroxide and carbon dioxide appropriately react with each other, and thus calcium carbonate is efficiently produced.

Further, in the method for producing calcium carbonate according to the present invention, it is preferable that a water content of the raw material in the reaction step is lower than a water content of the raw material in the preparation step. Moreover, in the method for producing calcium carbonate according to the present invention, a content of calcium hydroxide in solid of the raw material is preferably 30% or more. Furthermore, in the method for producing calcium carbonate according to the present invention, a content of carbon dioxide in the gas is preferably 5% or more. Further, in the method for producing calcium carbonate according to the present invention, an atmospheric temperature in the reaction step is preferably 10 to 75°C. In the method for producing calcium carbonate according to the present invention, the raw material is preferably carbide slag, waste concrete, sludge of ready mixed concrete, cement, or a mixture thereof.

The present invention enables to more reliably achieve excellent production efficiency of calcium carbonate.

## EFFECT OF THE INVENTION

[0008]

According to the method for producing calcium carbonate of the present invention, calcium carbonate can be produced with excellent production efficiency.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

[FIG. 1] FIG. 1 is a graph showing a solid phase constitution and changes with time of a water content of Sample 1 in Example 1.

[FIG. 2] FIG. 2 is a graph showing a solid phase constitution and changes with time of a water content of Sample 2 in Example 1.

[FIG. 3] FIG. 3 is a graph showing a solid phase constitution and changes with time of a water content of Sample 3 in Example 2.

[FIG. 4] FIG. 4 is a graph showing changes with time in solid phase constitutions of Samples 4, 5, and 6 in Example 3.

[FIG. 5] FIG. 5 is a graph showing changes with time in solid phase constitutions of Samples 7, 8, and 9 in Example 4.

[FIG. 6] FIG. 6 is a graph showing changes with time in solid phase constitutions of Samples 10, 11, 12, and 13 in Example 5.

[FIG. 7] FIG. 7 is a graph showing changes with time in a solid phase constitution of Sample 14 in Example 6.

## EMBODIMENT FOR CARRYING OUT INVENTION

[0010]

Hereinafter, an embodiment for carrying out a method for producing calcium carbonate according to the present invention (i.e., a method for producing calcium carbonate according to the present embodiment) will be described.

The method for producing calcium carbonate according to the present embodiment includes a preparation step and a reaction step, and may include a drying step after the reaction step.

Hereinafter, each step will be described in detail.

[0011]

[Preparation Step]

In the preparation step, a raw material used in the reaction step described later is prepared.

(Preparation Step: Raw Material)

The raw material prepared in the preparation step contains calcium hydroxide and has a water content within a predetermined range.

A content of calcium hydroxide in solid of the raw material (the solid when the raw material is dried at 105°C) is preferably 30% (specifically, w / w%) or more, more preferably 50% or more, 70% or more, 80% or more, or 90% or more. When the content of calcium hydroxide is equal to or more than a predetermined value, production efficiency of calcium carbonate in a product obtained in the reaction step described later can be made excellent.

A water content of the raw material in the preparation step (in other words, a water content of the raw material at the starting time of the reaction step) is preferably 0.3 to 40% (specifically, w / w%), more preferably 1 to 40%, 5 to 30%, or 10 to 25% on a wet basis (WB). By setting the water content of the raw material within a predetermined range in the preparation step, the carbonation reaction of calcium hydroxide rapidly proceeds in the reaction step described later, and the production amount of calcium carbonate within a predetermined time increases.

The raw material is not particularly limited as long as it satisfies the above two requirements, and examples thereof include sludge (carbide slag) produced as a by-product in the step of producing acetylene gas from calcium carbide, waste concrete, sludge of ready mixed concrete, cement, and the like, and one or more of these can be appropriately pulverized and used. Among these, it is particularly preferable to use carbide slag which is a by-product (residue) and has a high content of calcium hydroxide.

[0012]

(Preparation Step: Adjustment of Water Content)

When a water content of the raw material is high, the raw material may be subjected to a dehydration treatment so that the water content falls within the above described range. Examples of the dehydration treatment include thickening, filter pressing, centrifuging, gravitational settling, heat drying, and natural drying. Here, one or more of these treatments may be performed, and thickening and filter pressing are preferable from the viewpoint of energy efficiency and work efficiency.

When a water content of the raw material is low, the raw material may be subjected to a hydration treatment so that the water content falls within the above described range. The water used in the hydration treatment is not particularly limited. For example, tap water, distilled water, ion exchanged water, RO water, a solution separated in the dehydration treatment described above, or the like may be used.

[0013]

[Reaction Step]

In the reaction step, a gas is supplied to the raw material, and calcium hydroxide contained in the raw material and carbon dioxide contained in the gas are made to react with each other to produce calcium carbonate.

(Reaction Step: Adjustment of Water content)

The water content of the raw material in the reaction step is preferably in the range of 0.3 to 40%, more preferably 1 to 40%, 5 to 30%, or 10 to 20%. By setting the water content of the raw material in the reaction step within a predetermined range, the carbonation reaction of calcium hydroxide appropriately proceeds, and a produced amount of calcium carbonate within a predetermined time increases.

Further, in the reaction step, a temperature of the raw material rises due to generation of reaction heat associated with the reaction of "$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$". As a result, water evaporates from the raw material, and the water content of the raw material gradually decreases. Therefore, the raw material may be appropriately subjected to a hydration treatment so that the water content of the raw material is within the above described range. When considering evaporation of water in the reaction, the water content of the raw material in the reaction step becomes lower than the water content of the raw material in the preparation step unless an extreme hydration treatment is performed.

Measurement of the water content of the raw material in the reaction step may be performed at predetermined time intervals (for example, at intervals of 5 to 40 minutes, or at intervals of 15 to 30 minutes), and TG-DTA may be used. Alternatively, a predetermined amount of the raw material may be taken out therefrom during the reaction step, and the water content may be calculated based on a moisture meter or a change in mass before and after heating and drying (for example, heating at 105°C or higher for 1 hour or longer).

Then, based on the calculated water content of the raw material, a hydration treatment may be performed as appropriate. Further, based on the reduction rate of the water content of the raw material obtained in advance, the hydration treatment may be appropriately performed. Water used in the hydration treatment is as described in the preparation step.

[0014]

(Reaction Step: Gas)

A gas used in the reaction step contains carbon dioxide. As the gas, an exhaust gas (having a carbon dioxide concentration of about 10%) from a boiler or the like, a carbon dioxide gas highly concentrated by a concentrator, or the like can be used.

From the viewpoint of the production rate of calcium carbonate, a content of carbon dioxide in the gas may be 5% (specifically, v / v%) or more. When the content of carbon dioxide in the gas is 5% or more, the carbonation reaction can be rapidly advanced to produce calcium carbonate in a short time, and therefore, energy required for production can be reduced.

On the other hand, from the viewpoint of the production rate of calcium carbonate, the content of carbon dioxide in the gas is preferably higher, but based on the results of FIG. 6 and the like described later, even if the content of carbon dioxide is too high, the final production amount of calcium carbonate does not change much. Therefore, from the economical viewpoint, the exhaust gas may be used as it is, or a $CO_2$ gas concentrated for efficient transportation of the exhaust gas or for use in industries requiring high concentration and high purity $CO_2$ may be used.

A supply amount of the gas may be appropriately set depending on the amount of the raw material to be used, the content of carbon dioxide in the gas, and the like, and, for example, is 20 to 100L / min (preferably 50 to 75L / min), when the raw material is approximately 6kg. Therefore, when the raw material to be used is Zkg, the supply amount of the gas is [3.33 × Z] to [16.6 × Z] L / min (preferably [8.33 × Z] to [12.5 × Z] L / min).

A time for supplying the gas (time for the reaction step) depends on the progress of the reaction, but is, for example, 10 to 130 minutes (preferably 60 to 120 minutes) when the reaction step is performed under the above described conditions.

[0015]

(Reaction Step: Other Conditions)

In the reaction step, the gas is supplied to the raw material while stirring the raw material in order to bring the raw material and the gas into contact with each other. The stirring is not

particularly limited in strength, method, and the like as long as the raw material and the gas are appropriately brought into contact with each other, and may be performed with a known stirrer. Further, since any apparatus having a stirring function may be used, a closed stirrer, a dryer having a stirring function, or the like may be used.

An atmospheric temperature in the reaction step is not particularly limited as long as it is in the range of 10 to 75°C, and from the viewpoint of energy efficiency, room temperature (for example, 20 to 50°C) at which a treatment such as heating is not performed is preferable.

[0016]

[Drying Step]

In the drying step, the product containing calcium carbonate obtained in the reacting step is subjected to a drying treatment as necessary so that, for example, the water content (the term according to JIS S is "moisture content") becomes 1.0% or less as shown in JIS A 6201 "Fly ashes for concrete" and JIS A5 041 "Crushed stone powders for concrete". Note, the drying treatment may be performed by a known treatment such as heat drying, natural drying, or reduced pressure drying. A time and intensity of the drying treatment may be appropriately set according to the needs for the product (the time of the treatment may be increased or the intensity of the treatment may be increased when a product having a low water content is required).

## EXAMPLES

[0017]

[Example 1]

In Example 1, the influence of the replenishment of water

evaporated in the reaction step was confirmed.

(Test Content)

As a raw material of Samples 1 and 2, a slurry of carbide slag (the content of solid in the slurry: about 20%, the content of calcium hydroxide in the solid: 86.9%), which is a by-product generated when acetylene is produced by making calcium carbide react with water, was used.

First, slurry filtration was performed on each raw material to adjust the water content of the raw material to 44.3% (WB). Thereafter, each of the raw materials was allowed to stand for 5 hours on a tray in an incubator of a neutralization acceleration tester (MIT-639-3-05 manufactured by Marui Co., Ltd.) under conditions of a temperature of 50°C, RH of 60%, and a $CO_2$ concentration of 5%. Then, a sample for measurement was collected from each sample every hour from the start of the standing storage, and the collected sample was measured with a simultaneous thermogravimetry / differential thermal analyzer (TG-DTA: Thermo Mass Photo manufactured by Rigaku Corporation).

For Sample 1, water was supplied to the raw material at the time of measurement in an amount corresponding to the amount of water that was vaporized and confirmed at the time of sampling by TG-DTA (that is, water was supplied so that the water content of the raw material was 44.3%), and water was mixed into the entire raw material. On the other hand, in Sample 2, no water was supplied to the raw material during the standing period.

Note, the water content of each sample was calculated based on the mass change before and after drying by putting a sample taken from each sample into a drying machine (drying temperature: 105°C) and drying the sample for 24 hours or more.

[0018]

(Measurement Method of TG-DTA)

In the TG-DTA measurement, about 30mg of the collected sample was placed in a platinum cell, and heated from 20°C to 1000°C at a temperature rising rate of 20°C / min while flowing nitrogen at 30 0mL / min to obtain a TG curve and a DTA curve, and then the measurement results shown in the table were obtained.

[0019]

(Calculation Method of Each Index)

Each index shown in the table was calculated by the following method using each measurement result of TG-DTA.

"$Ca(OH)_2$ (%: anhydride equivalent)" = "CH weight loss (%)" / 18 × 74 × 100 / (100 - "water content (%) at 300°C or less") "

"$CaCO_3$ (%: anhydride equivalent)" = "$CaCO_3$ weight loss (%) "/ 44 × 100 × 100 / (100 - "water content (%) at 300°C or less ")"

"Others (%: anhydride equivalent)" = 100 - "$Ca(OH)_2$ (%: anhydride equivalent)" - "$CaCO_3$ (%: anhydride equivalent)"

"CaO total (%: anhydride equivalent)" = "$Ca(OH)_2$ (%: anhydride equivalent)" / 74 × 56 + “$CaCO_3$ (%: anhydride equivalent)" / 100 × 56

“$Ca(OH)_2$ (%: initial CaO content equivalent)” = “$Ca(OH)_2$ (%: anhydrate equivalent)” / “CaO total (%: anhydride equivalent) × “CaO total in raw material before reaction (%: anhydride equivalent)”

“CaCO3 (%: initial CaO content equivalent)” = “$CaCO_3$ (%: anhydride equivalent)” / “CaO total (%: anhydride equivalent)” × “Cao total in raw material before rection (%: anhydride equivalent)”

“Others (%: initial CaO content equivalent)” = “others in raw material before reaction (%: anhydride equivalent)”

“Total (% initial CaO content equivalent)” = “$Ca(OH)_2$ (%:

initial CaO content equivalent)” + “$CaCO_3$ (%: initial CaO content equivalent)” + “others (%: initial CaO content equivalent)”

Here, the term "anhydride equivalent" refers to a content (%) of each component when the solid after removing water (such as adhering water) thus removed by heating to 300°C is 100%. The term "initial CaO content equivalent" refers to a content (%) of each component based on the initial (before reaction) CaO content, and is an index that can determine how much CaO initially present as $Ca(OH)_2$ has changed to CaO from $CaCO_3$ after the reaction. Further, "water content at 300°C or less" in the table is a content of water thus removed by heating to 300°C.

Note, the indices used in each figure are "$Ca(OH)_2$ (%: initial CaO content equivalent)", "$CaCO_3$ (%: initial CaO content equivalent)", "others (%: initial CaO content equivalent)", and a water content among the indices described above.

[0020]

[Table 1]

| | Reaction Time (hr) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Total Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Carbide Slag) | - | - | 20.51 | 1.76 | 26.5 | 24.7 | 2.93 | 86.9 | 4.1 | 9.0 | 68.0 | 65.7 | 2.3 | 9.0 | 77.1 | 68.0 |
| Sample 1 | 0 | 44.3 | - | - | - | - | - | 86.9 | 4.1 | 9.0 | 68.0 | 86.9 | 4.1 | 9.0 | 100.0 | 68.0 |
| | 1 | 44.3 | 20.6 | 1.4 | 26.5 | 25.0 | 2.87 | 87.2 | 3.4 | 9.4 | 67.9 | 87.4 | 3.4 | 9.0 | 99.8 | 68.0 |
| | 2 | 44.3 | 20.1 | 2.7 | 27.3 | 24.6 | 2.95 | 85.2 | 6.3 | 8.6 | 68.0 | 85.3 | 6.3 | 9.0 | 100.6 | 68.0 |
| | 3 | 44.3 | 19.5 | 3.5 | 27.2 | 23.7 | 2.96 | 82.4 | 8.3 | 9.3 | 67.0 | 83.7 | 8.4 | 9.0 | 101.1 | 68.0 |
| | 4 | 44.3 | 19.3 | 4.1 | 27.7 | 23.6 | 2.93 | 81.7 | 9.7 | 8.6 | 67.2 | 82.7 | 9.8 | 9.0 | 101.5 | 68.0 |
| | 5 | 44.3 | 19.1 | 4.6 | 27.8 | 23.3 | 2.97 | 80.8 | 10.7 | 8.6 | 67.1 | 81.9 | 10.8 | 9.0 | 101.7 | 68.0 |
| Sample 2 | 0 | 44.3 | - | - | - | - | - | 86.9 | 4.1 | 9.0 | 68.0 | 86.9 | 4.1 | 9.0 | 100.0 | 68.0 |
| | 1 | 35.5 | 19.6 | 3.09 | 27.3 | 24.2 | 3.21 | 83.4 | 7.3 | 9.4 | 67.2 | 84.5 | 7.4 | 9.0 | 100.8 | 68.0 |
| | 2 | 26.3 | 19.2 | 4.75 | 28.2 | 23.4 | 3.07 | 81.3 | 11.1 | 7.6 | 67.8 | 81.6 | 11.2 | 9.0 | 100.8 | 68.0 |
| | 3 | 9.6 | 3.8 | 32.83 | 42.2 | 9.4 | 3.53 | 16.4 | 77.3 | 6.3 | 55.7 | 20.0 | 94.5 | 9.0 | 123.5 | 68.0 |
| | 4 | 0.2 | 2.5 | 36.23 | 43.5 | 7.3 | 3.11 | 10.6 | 85.0 | 4.5 | 55.6 | 12.9 | 104.0 | 9.0 | 126.0 | 68.0 |
| | 5 | 0.2 | 2.4 | 36.03 | 43.6 | 7.5 | 3.23 | 10.3 | 84.6 | 5.1 | 55.2 | 12.7 | 104.4 | 9.0 | 126.1 | 68.0 |

Red.Cont.: Reduction Content

[0021]

(Examination of Results in Example 1)

FIG. 1 is a graph showing a solid phase constitution and changes with time of the water content of Sample 1 in Example 1. FIG. 2 is a graph showing a solid phase constitution and changes with time of the water content of Sample 2 in Example 1.

Based on the results of FIG. 1 and Table 1, in Sample 1 in which water was supplied in the reaction step, the water content of the raw material was always high (more than 40%), and therefore, the reaction of calcium hydroxide did not occur, and the proportion of calcium carbonate in the solid phase constitution was very small.

On the other hand, based on the results of FIG. 2 and Table 1, in Sample 2 in which water was not supplied in the reaction step, a rate of calcium carbonate in the solid phase constitution was significantly increased after 2 hours when the water content in the raw material was decreased.

Based on these results, it was confirmed that the water content of the raw material in the reaction step has a very large influence on the produced amount of calcium carbonate.

Note, after removing the adhered water by anhydride conversion, the initial CaO content equivalent is based on the CaO content before the start of the reaction, and the CaO content is also converted to the initial CaO content equivalent at each reaction period. Therefore, the content of each component at each reaction period exceeds 100% by the content of $CO_2$ absorbed by the reaction.

[0022]

[Example 2]

In Example 2, the influence of performing the drying

treatment in the reaction step was confirmed.

(Test Content)

As a raw material of Sample 3, calcium hydroxide (commercially available product) shown in Table 2 was used.

First, water (tap water) was added to the raw material to adjust the water content of the raw material to 40.0% (WB). Thereafter, reaction treatment was performed for 60 minutes while stirring the raw material (approximately 6kg) using a paddle mixer (NPD-1. 6W-12L-G, manufactured by Nara Machinery Co., Ltd.) and supplying a gas having a $CO_2$ content of 20% at 250L / min. Note, during the reaction treatment of Example 2, drying by a paddle mixer (circulation of water vapor at 110°C through the wall surface (jacket) of the container of the dryer) was performed. Then, before the reaction treatment and 10 minutes, 20 minutes, 35 minutes, and 55 minutes after the start of the reaction treatment, the water content of the sampled raw material was measured with an infrared moisture meter (FD - 800 manufactured by Kett Electric Laboratory, drying temperature: 105°C), and each index such as the content of calcium hydroxide and the content of calcium carbonate was measured with TG-DTA (the same apparatus as in Example 1).

In the case of Sample 3, no water was supplied to the raw material during the reaction period.

Note, the measurement method by TG-DTA and the calculation method of each index were the same as those in Example 1.

[0023]

Table 2

| | Reaction Time (min) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Ca(OH)2 Comertial Product) | - | - | 21.8 | 2.22 | 25.41 | 23.19 | 1.05 | 90.5 | 5.1 | 4.4 | 71.4 | 68.5 | 2.9 | 4.4 | 75.7 | 71.4 |
| Sample 3 | 0 | 40.0 | - | - | - | - | - | 90.5 | 5.1 | 4.4 | 71.4 | 90.5 | 5.1 | 4.4 | 100.0 | 71.4 |
| | 10 | 32.2 | 20.4 | 5.52 | 27.290 | 21.8 | 0.92 | 84.8 | 12.7 | 2.5 | 71.3 | 84.9 | 12.7 | 4.4 | 102.0 | 71.4 |
| | 20 | 21.8 | 16.0 | 13.25 | 30.920 | 17.7 | 1.05 | 66.4 | 30.4 | 3.2 | 67.3 | 70.4 | 32.3 | 4.4 | 107.1 | 71.4 |
| | 35 | 7.1 | 9.1 | 25.66 | 37.240 | 11.6 | 1.28 | 38.1 | 59.1 | 2.9 | 61.9 | 43.9 | 68.1 | 4.4 | 116.4 | 71.4 |
| | 55 | 0.5 | 7.3 | 29.18 | 38.860 | 9.7 | 1.24 | 30.4 | 67.1 | 2.4 | 60.6 | 35.8 | 79.0 | 4.4 | 119.2 | 71.4 |

Red.Cont: Reduction Content

[0024]

(Examination of Results in Example 2)

FIG. 3 is a graph showing a solid phase constitution and changes with time of the water content of Sample 3 in Example 2.

Based on the results of FIG. 3 and Table 2, it was confirmed that the proportion of calcium carbonate in the solid phase constitution increased as the water content of the raw material decreased in the reaction step. When the results of Sample 3 shown in FIG. 3 and Sample 2 shown in FIG. 2 were compared, it was found that the time until calcium carbonate was produced was significantly shortened in Sample 3 in which the raw materials reacted while being stirred.

However, the present inventors considered that there is room for further improvement in order to further increase the proportion of the solid phase constitution of calcium carbonate in the product.

[0025]

[Example 3]

In Example 3, the influence of the water content of the raw material was confirmed.

(Test Content)

As raw materials of Samples 4, 5, and 6, calcium hydroxide (commercially available product) shown in Table 3 was used.

First, water (tap water) was added to each raw material, and a water content of the raw material of Sample 4 was set to 10% (WB), a water content of the raw material of Sample 5 was set to 20% (WB), and a water content of the raw material of Sample 6 was set to 30% (WB). Thereafter, while stirring the respective raw materials 6kg using a paddle mixer (the same device as in Example 2), a reaction treatment was carried out for 90 minutes while

supplying a gas having a $CO_2$ content of 20% at 50L / min. During the reaction treatment of Example 3, the temperature control of heating and cooling was not performed, but the temperature (ambient temperature) in the paddle mixer was 20 to 50°C. Then, before the reaction treatment and after 30 minutes, 60 minutes, and 90 minutes from the start of the reaction treatment, the water content of each of the sampled raw materials was measured with an infrared moisture meter (the same apparatus as in Example 2), and each index was measured with TG-DTA (the same apparatus as in Example 1).

For Samples 4, 5, and 6, water was supplied to the raw material by the amount of water evaporated confirmed at the time of measurement of the water content (that is, water was supplied so that the water content of the raw material was 10% for Sample 4, 20% for Sample 5, and 30% for Sample 6).

Note, the measurement method by TG-DTA and the calculation method of each index were the same as those in Example 1.

[0026]

Table 3

| | Reaction Time (min) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Ca(OH)2 Comertial Product) | - | - | 21.8 | 2.22 | 25.41 | 23.19 | 1.05 | 90.5 | 5.1 | 4.4 | 71.4 | 68.5 | 2.9 | 4.4 | 75.7 | 71.4 |
| Sample 4~6 | 0 | - | - | - | - | - | - | 90.5 | 5.1 | 4.4 | 71.4 | 90.5 | 5.1 | 4.4 | 100.3 | 71.4 |
| Sample 4 | 30 | 10 (7.1) | 12.78 | 19.14 | 34.05 | 14.9 | 1.75 | 53.5 | 44.3 | 2.2 | 65.3 | 58.5 | 48.4 | 4.4 | 111.3 | 71.4 |
| | 60 | 10 (7.7) | 5.09 | 32.77 | 40.46 | 7.7 | 2.06 | 21.4 | 76.0 | 2.6 | 58.8 | 26.0 | 92.4 | 4.4 | 122.7 | 71.4 |
| | 90 | 10 (12.3) | 1.11 | 40.3 | 43.84 | 3.5 | 1.81 | 4.6 | 93.3 | 2.1 | 55.8 | 5.9 | 119.4 | 4.4 | 129.7 | 71.4 |
| Sample 5 | 30 | 20 (13.4) | 9.88 | 24.24 | 36.49 | 12.3 | 1.86 | 41.4 | 56.1 | 2.5 | 62.8 | 47.1 | 63.8 | 4.4 | 115.3 | 71.4 |
| | 60 | 20 (21.6) | 3.95 | 34.99 | 41.45 | 6.5 | 1.89 | 16.6 | 81.1 | 2.4 | 57.9 | 20.4 | 99.9 | 4.4 | 124.5 | 71.4 |
| | 90 | 20 (21.6) | 2.17 | 38.53 | 43.25 | 4.7 | 1.88 | 9.1 | 89.2 | 1.7 | 56.9 | 11.4 | 112.0 | 4.4 | 127.8 | 71.4 |
| Sample 6 | 30 | 30 (28.2) | 11.94 | 20.61 | 34.83 | 14.2 | 1.78 | 50.0 | 47.7 | 2.3 | 64.5 | 55.3 | 52.7 | 4.4 | 112.4 | 71.4 |
| | 60 | 30 (29.7) | 8.49 | 26.94 | 38.24 | 11.3 | 2.19 | 35.7 | 62.6 | 1.7 | 62.1 | 41.0 | 72.0 | 4.4 | 117.4 | 71.4 |
| | 90 | 30 (26.6) | 5.42 | 31.94 | 40.72 | 8.8 | 2.45 | 22.8 | 74.4 | 2.7 | 59.0 | 27.6 | 90.1 | 4.4 | 122.1 | 71.4 |

Red.Cont.: Reduction Content

[0027]

(Examination of Results in Example 3)

FIG. 4 is a graph showing changes with time in the solid phase constitution of Samples 4, 5, and 6 in Example 3.

Based on the results of FIG. 4 and Table 3, it was confirmed that the rate of calcium carbonate in the solid phase constitution was considerably increased in a short time of 30 to 90 minutes by controlling a water content of the raw material within a predetermined range in the reaction step. In other words, it was confirmed that according to the present invention, the amount of calcium carbonate produced within a predetermined time was increased, and excellent production efficiency could be exerted.

Although good results were obtained for all of Samples 4, 5, and 6, very favorable results were obtained particularly for Samples 4 and 5.

Note, the numerical values in parentheses in the lower part of the water content in Table 3 are the water content of the raw material immediately before water is supplied, and the numerical values in the upper part of the water content are the target values, and the same applies to Tables 4 and 5 described later.

[0028]

[Example 4]

In Example 4, the influence of the ambient temperature in the reaction step was confirmed.

(Test Content)

As the raw materials of Samples 7, 8, and 9, calcium hydroxide (commercially available product) shown in Table 4 was used.

First, water (tap water) was added to each raw material, and

a water content of the raw material of Sample 7 was set to 10% (WB), a water content of the raw material of Sample 8 was set to 20% (WB), and a water content of the raw material of Sample 9 was set to 30% (WB). Thereafter, while stirring the respective raw materials 6kg using a paddle mixer (the same device as in Example 2), a reaction treatment was carried out for 90 minutes while supplying a gas having a $CO_2$ content of 20% at 50L / min. During the reaction treatment of Example 4, the temperature (ambient temperature) in the paddle mixer was controlled to be approximately 70 to 90°C. Then, before the reaction treatment and after 30 minutes, 60 minutes, and 90 minutes from the start of the reaction treatment, the water content of each of the sampled raw materials was measured with an infrared moisture meter (the same apparatus as in Example 2), and each index was measured with TG-D18TA (the same apparatus as in Example 1).

For samples 7, 8, and 9, water was supplied to the raw material by the amount of evaporated water confirmed at the time of measurement of the water content (that is, water was supplied so that the water content of the raw material was 10% for sample 7, 20% for sample 8, and 30% for sample 9).

Note, the measurement method by TG-DTA and the calculation method of each index were the same as those in Example 1.

[0029]

Table 4

| | Reaction Time (min) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Ca(OH)2 Comertial Product) | - | - | 21.8 | 2.22 | 25.41 | 23.19 | 1.05 | 90.5 | 5.1 | 4.4 | 71.4 | 68.5 | 2.9 | 4.4 | 75.7 | 71.4 |
| Sample 7~9 | 0 | - | - | - | - | - | - | 90.5 | 5.1 | 4.4 | 71.4 | 90.5 | 5.1 | 4.4 | 100.3 | 71.4 |
| Sample 7 | 30 | 10 (0.6) | 13.3 | 18.7 | 33.3 | 14.6 | 0.98 | 55.1 | 42.9 | 2 | 65.7 | 59.8 | 46.6 | 4.4 | 110.8 | 71.4 |
| | 60 | 10 (0.5) | 9.5 | 25.5 | 36.2 | 10.7 | 0.87 | 39.3 | 58.5 | 2.2 | 62.5 | 44.9 | 66.8 | 4.4 | 116.0 | 71.4 |
| | 90 | 10 (0.5) | 5.1 | 33.4 | 39.8 | 6.4 | 0.89 | 21.2 | 76.6 | 2.1 | 59.0 | 25.7 | 92.7 | 4.4 | 122.3 | 71.4 |
| Sample 8 | 30 | 20 (2.7) | 12.6 | 19.8 | 33.9 | 14.1 | 1.05 | 52.3 | 45.5 | 2.2 | 65.0 | 57.4 | 49.9 | 4.4 | 111.5 | 71.4 |
| | 60 | 20 (4.6) | 8.0 | 28.4 | 38.0 | 9.5 | 1.06 | 33.3 | 65.3 | 1.4 | 61.8 | 38.5 | 75.5 | 4.4 | 118.3 | 71.4 |
| | 90 | 20 (5.5) | 2.7 | 38.2 | 42.3 | 4.1 | 0.85 | 11.0 | 87.5 | 1.5 | 57.3 | 13.7 | 109.0 | 4.4 | 127.0 | 71.4 |
| Sample 9 | 30 | 30 (19.6) | 13.4 | 18.2 | 33.3 | 15.2 | 1.20 | 55.7 | 41.8 | 2.5 | 65.6 | 60.6 | 45.5 | 4.4 | 110.5 | 71.4 |
| | 60 | 30 (19.0) | 8.7 | 27.0 | 37.4 | 10.5 | 1.14 | 36.3 | 62.0 | 1.8 | 62.1 | 41.6 | 71.2 | 4.4 | 117.2 | 71.4 |
| | 90 | 30 (17.5) | 4.2 | 35.3 | 41.2 | 6.0 | 1.11 | 17.3 | 81.0 | 1.6 | 58.5 | 21.2 | 98.9 | 4.4 | 124.4 | 71.4 |

Red.Cont.: Reduction Content

[0030]

(Examination of Results in Example 4)

FIG. 5 is a graph showing changes with time of the solid phase constitution of Samples 7, 8, and 9 in Example 4.

Based on the results of FIG. 5 and Table 4, it was confirmed that the rate of calcium carbonate in the solid phase constitution can be increased in a short time of 30 to 90 minutes even when the atmospheric temperature of the reaction step is controlled to 70 to 90°C.

However, when Samples 7, 8, and 9 shown in FIG. 5 were compared with Samples 4, 5, and 6 shown in FIG. 4, the latter group in which the ambient temperature was 20 to 50°C had a slightly higher proportion of calcium carbonate in the solid phase constitution. Therefore, it was confirmed that it is not necessary to intentionally control the ambient temperature of the reaction step to be high from the viewpoint of energy efficiency.

[0031]

[Example 5]

In Example 5, the influence of the content of carbon dioxide in the gas was confirmed.

(Test Content)

As the raw materials of Samples 10, 11, 12, and 13, calcium hydroxide (commercially available product) shown in Table 5 was used.

First, water (tap water) was added to each raw material to adjust the water content of each raw material to 20% (WB). Thereafter, while stirring each of the raw materials 6kg using a paddle mixer (the same device as in Example 2), a reaction treatment was performed for 60 minutes (90 minutes only for Samples 10 and 11) while supplying a gas having a $CO_2$ content of 10% for

Sample 10, a gas having a $CO_2$ content of 20% for Sample 11, a gas having a $CO_2$ content of 50% for Sample 12, and a gas having a $CO_2$ content of 100% for Sample 13 at 50L / min. During the reaction treatment in Example 5, temperature control such as heating and cooling was not performed, but the temperature (ambient temperature) in the paddle mixer was 20 to 50°C. Then, before the reaction treatment and after 15 minutes, 30 minutes, 60 minutes, and 90 minutes from the start of the reaction treatment (only for the Samples 10 and 11), the water content of each of the sampled raw materials was measured by the infrared moisture meter (the same device as in Example 2), and each index was measured by TG-DTA (the same device as in Example 1).

For Samples 10, 11, 12, and 13, water was supplied to the raw materials by the amount of evaporated water confirmed at the time of measurement of the water content (that is, water was supplied such that the water content of each raw material was 20%).

Note, the measurement method by TG-DTA and the calculation method of each index were the same as those in Example 1.

[0032]

Table 5

| | Reaction Time (min) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Ca(OH)2 Comertial Product) | - | - | 21.8 | 2.22 | 25.41 | 23.19 | 1.05 | 90.5 | 5.1 | 4.4 | 71.4 | 68.5 | 2.9 | 4.4 | 75.7 | 71.4 |
| Sample 10~13 | 0 | - | - | - | - | - | - | 90.5 | 5.1 | 4.4 | 71.4 | 90.5 | 5.1 | 4.4 | 100.0 | 71.4 |
| Sample 10 | 15 | | 15.72 | 13.5 | 31.25 | 17.8 | 1.86 | 65.9 | 31.3 | 2.9 | 67.3 | 69.8 | 33.1 | 4.4 | 107.3 | 71.4 |
| | 30 | 20 (15.68) | 13.77 | 17.34 | 33.34 | 16.0 | 1.86 | 57.7 | 40.2 | 2.2 | 66.1 | 62.2 | 43.3 | 4.4 | 109.9 | 71.4 |
| | 60 | 20 (20.93) | 10.62 | 23.04 | 36.25 | 13.2 | 1.89 | 44.5 | 53.4 | 2.1 | 63.6 | 50.0 | 59.9 | 4.4 | 114.3 | 71.4 |
| | 90 | 20 (20.73) | 6.43 | 31.02 | 40.16 | 9.1 | 1.88 | 26.9 | 71.9 | 1.2 | 60.6 | 31.7 | 84.6 | 4.4 | 120.7 | 71.4 |
| Sample 11 | 15 | 20 (10.6) | 11.18 | 20.92 | 34.61 | 13.7 | 2.05 | 46.9 | 48.5 | 4.5 | 62.7 | 53.4 | 55.3 | 4.4 | 113 | 71.4 |
| | 30 | 20 (12.0) | 3.6 | 34.96 | 41.66 | 6.7 | 2.55 | 15.2 | 81.5 | 3.3 | 57.1 | 19.0 | 101.8 | 4.4 | 125.1 | 71.4 |
| | 60 | 20 (19.4) | 1.21 | 38.86 | 43.51 | 4.6 | 2.69 | 5.1 | 90.8 | 4.1 | 54.7 | 6.7 | 118.4 | 4.4 | 129.5 | 71.4 |
| | 90 | 20 (19.6) | 0.49 | 39.85 | 44.30 | 4.4 | 2.92 | 2.1 | 93.3 | 4.6 | 53.8 | 2.8 | 123.7 | 4.4 | 130.8 | 71.4 |
| Sample 12 | 15 | 20 (6.5) | 3.45 | 35.76 | 41.44 | 5.7 | 1.67 | 14.4 | 82.7 | 2.9 | 57.2 | 18.0 | 103.1 | 4.4 | 125.5 | 71.4 |
| | 30 | 20 (12.3) | 2.84 | 36.58 | 42.48 | 5.7 | 2.28 | 11.9 | 85.1 | 3.0 | 56.7 | 15.0 | 107.1 | 4.4 | 126.5 | 71.4 |
| | 60 | 20 (19.0) | 2.44 | 36.97 | 42.24 | 5.3 | 2.14 | 10.3 | 85.9 | 3.9 | 55.8 | 13.1 | 109.7 | 4.4 | 127.2 | 71.4 |
| Sample 13 | 15 | 20 (10.6) | 3.87 | 34.72 | 40.68 | 6.0 | 1.45 | 16.1 | 80.1 | 3.8 | 57.1 | 20.2 | 100.2 | 4.4 | 124.7 | 41.4 |
| | 30 | 20 (11.5) | 3.6 | 35.26 | 41.17 | 5.9 | 1.73 | 15.1 | 81.5 | 3.4 | 57.1 | 18.8 | 102.0 | 4.4 | 125.2 | 71.4 |
| | 60 | 20 (17.8) | 2.24 | 37.33 | 420.7 | 4.7 | 1.85 | 9.4 | 86.4 | 4.2 | 55.5 | 12.1 | 111.1 | 4.4 | 127.6 | 71.4 |

Red.Cont.: Reduction Content

[0033]

(Examination of Results in Example 5)

FIG. 6 is a graph showing changes with time in the solid phase constitution of Samples 10, 11, 12, and 13 in Example 5.

Based on the results of FIG. 6 and Table 5, it was confirmed that the higher the content of carbon dioxide in the gas to be supplied, the faster the reaction occurred, and the rate of calcium carbonate in the solid phase constitution could be increased in a shorter time.

Note that, when Sample 12 in which the content of carbon dioxide in the gas to be supplied was 50% and Sample 13 in which the content of carbon dioxide in the gas to be supplied was 100% were compared, no large difference was confirmed, and thus it was found that the effect of speeding up the reaction was sufficiently exhibited when the content of carbon dioxide was about 50%.

[0034]

[Example 6]

In Example 6, the influence of using carbide slag as a raw material was confirmed.

(Test Content)

As a raw material of Sample 14, carbide slag (content of calcium hydroxide in solid: about 86%) shown in Table 6 was used.

First, slurry filtration was performed on the raw material to adjust the water content of the raw material to 37.7% (WB). Thereafter, while stirring the raw material 5kg using a PAMAX mixer (WB-20V manufactured by Pacific Machinery Co., Ltd.), a reaction treatment was carried out for 120 minutes while supplying a gas having a $CO_2$ content of 20% at a 50L / min. During the reaction treatment in Example 6, the drying treatment by the mixer was not performed, and the atmospheric temperature was not controlled.

Then, before the reaction treatment and 30 minutes, 60 minutes, 90 minutes, and 120 minutes after the start of the reaction treatment, the water content of the sampled raw material was measured with an infrared moisture meter (the same apparatus as in Example 2), and each index was measured with TG-DTA (the same apparatus as in Example 1).

For Sample 14, no water was supplied to the feedstock during the reaction period.

Note, the measurement method by TG-DTA and the calculation method of each index were the same as those in Example 1.

[0035]

Table 6

| | Reaction Time (hr) | Water Content | TG-DTA Measurement (Measurement Results) | | | | | Anhydride Equivalent (%) | | | | Initial CaO Content Equivalent (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | CH | $CaCO_3$ | Total Red.Cont | Total Water Content | Water Content (%) | $Ca(OH)_2$ | $CaCO_3$ | Others | CaO total | $Ca(OH)_2$ | $CaCO_3$ | Others | Total | CaO Total (Check) |
| | | WB(%) | Red.Cont (%) | Red.Cont (%) | (%) | (%) | ≤300°C | | | | | | | | | |
| Raw Material (Carbide Slag) | - | - | 20.4 | 1.4 | 26.05 | 24.7 | 2.89 | 86.4 | 3.3 | 10.4 | 67.2 | 86.4 | 3.3 | 10.4 | 100.0 | 67.2 |
| Sample 14 | 0 | 37.7 | - | - | - | - | - | 86.4 | 3.3 | 10.4 | 67.2 | 86.4 | 3.3 | 10.4 | 100.0 | 67.2 |
| | 30 | 31.8 | 12.94 | 15.7 | 32.96 | 17.3 | 3.47 | 55.1 | 36.9 | 8.0 | 62.4 | 59.4 | 39.7 | 10.4 | 109.5 | 67.2 |
| | 60 | 28.6 | 6.46 | 27.7 | 38.92 | 11.2 | 3.82 | 27.6 | 65.5 | 6.9 | 57.6 | 32.2 | 76.4 | 10.4 | 119.0 | 67.2 |
| | 90 | 25.8 | 1.81 | 35.9 | 42.76 | 6.8 | 3.65 | 7.7 | 84.7 | 7.5 | 53.3 | 9.7 | 106.8 | 10.4 | 126.9 | 67.2 |
| | 120 | 24.3 | 0.37 | 39.4 | 44.15 | 4.7 | 3.00 | 1.6 | 92.4 | 6.1 | 52.9 | 2.0 | 117.3 | 10.4 | 129.6 | 67.2 |

Red.Cont.: Reduction Content

[0036]

(Examination of Results in Example 6)

FIG. 7 is a graph showing changes with time of the solid phase constitution of Sample 14 in Example 6.

Based on the results of FIG. 7 and Table 6, it was confirmed that the rate of calcium carbonate in the solid phase constitution can be sufficiently increased even when the carbide slag is used as the raw material.

Further, based on the results of FIG. 7 and Table 6, it was confirmed that a preferable result was obtained even though water was not supplied to the raw material in the reaction step (even though the water content of the raw material was not controlled to be constant). Based on this result, it was found that in the present invention, it is not essential to control the water content of the raw material in the reaction step to be constant, but it is important that the water content of the raw material in the reaction step is within a predetermined range.

CLAIMS

[Claim 1] A method for producing calcium carbonate, comprising:

a preparation step of preparing a raw material containing calcium hydroxide and having a water content of 0.3 to 40%; and

a reaction step of supplying a gas containing carbon dioxide to the raw material while stirring the raw material and maintaining the water content of the raw material at 0.3 to 40%, thereby making the calcium hydroxide react with the carbon dioxide.

[Claim 2] The method for producing calcium carbonate according to claim 1, wherein a water content of the raw material in the reaction step is lower than a water content of the raw material in the preparation step.

[Claim 3] The method for producing calcium carbonate according to claim 1 or 2, wherein a content of calcium hydroxide in solid of the raw material is 30% or more.

[Claim 4] The method for producing calcium carbonate according to claim 1 or 2, wherein the gas has a carbon dioxide content of 5% or more.

[Claim 5] The method for producing calcium carbonate according to claim 1 or 2, wherein an atmospheric temperature in the reaction step is 10 to 75°C.

[Claim 6] The method for producing calcium carbonate according to claim 1 or 2, wherein the raw material is carbide slag, waste concrete, sludge of ready mixed concrete, cement, or a mixture

thereof.