

DESCRIPTION

Title of the Invention: FIXATION METHOD FOR CARBON DIOXIDE,
CARBON DIOXIDE-FIXED CEMENT HARDENED BODY, AND PRODUCTION
METHOD FOR SAME

TECHNICAL FIELD

[0001]

The present invention relates to a carbon dioxide fixation method, a carbon dioxide-fixed cement hardened body to which carbon dioxide is fixed by the fixation method, and a production method for same.

BACKGROUND ART

[0002]

There has been a request for decarbonization for decreasing emission of carbon dioxide, which is a type of greenhouse gas, to substantially zero to suppress the global warming. As the decarbonization goal, not only a technology for reducing carbon dioxide emission but also a carbon dioxide fixation (carbon fixation) technology for fixing emitted carbon dioxide into solids or liquids have attracted attentions.

[0003]

At construction sites, attempts have been made to fix carbon dioxide to concrete of architectural structures or civil engineering structures. To fix carbon dioxide into

concrete, conventional technologies utilizing neutralization/carbonation reactions have been used, in which carbon dioxide is supplied into a cement hardened body to produce calcium carbonate from a cement hydrate such as calcium hydroxide.

[0004]

However, if the carbon dioxide concentration is low, it takes a long time to fix carbon dioxide. When the carbon dioxide concentration is increased to shorten the fixation time, a risk of carbon dioxide leaking to the atmosphere is appeared, and therefore a sealed curing facility is required (see Patent Document 1). Therefore, carbon dioxide fixation has not yet been widely put to practical use.

[0005]

On the other hand, a liquid-phase carbonation method has also been investigated, in which carbon dioxide is fixed by supplied water which contains carbon dioxide gas (carbon dioxide) (e.g., carbonated water, nano-bubble carbonated water) to a cement hardened body (see Non-Patent Document 1). However, this method has a relatively low carbon dioxide fixation efficiency, because the amount of carbonate ion is decreased by decrease of pH when a large amount of carbon dioxide is dissolved in water.

Citation List

Patent Documents

[0006]

Patent Document 1: Japanese Unexamined Patent
Application, Publication No. 2023-022383
Non-Patent Documents

[0007]

Non-Patent Document 1: Shogo Katamura, Yosaku Ikee,
Yukiko Nishioka, and Yuto Takeuchi, "Modification of Recycled
Fine Aggregate by CO₂ Fixation, and Effects on fundamental
properties of Mortar", Japan Concrete Institute Annual
Collected Papers, Japan Concrete Institute, June 15, 2022,
Vol. 44, No. 1, p. 1186-1191

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0008]

A purpose of the present invention is to provide a carbon
dioxide fixation method capable of efficiently fixing carbon
dioxide to a cement hardened body, a carbon dioxide-fixed
cement hardened body to which carbon dioxide is fixed by the
fixation method, and a production method therefor.

Means for Solving the Problems

[0009]

The above purpose is achieved by the following examples
of the present invention. That means, examples of the present
invention are as follows.

<1>

A method for fixing carbon dioxide to a cement hardened body,
comprising supplying an aqueous solution of at least one

carbonate selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, and potassium bicarbonate to the cement hardened body.

<2>

The method according to <1>, in which the aqueous solution contains potassium carbonate, and a potassium carbonate concentration in the aqueous solution is 15 mass% or higher.

<3>

The method according to <1>, in which the method of supplying the aqueous solution to the cement hardened body comprises immersing the cement hardened body in the aqueous solution.

<4>

The method according to <1>, in which the method of supplying the aqueous solution to the cement hardened body comprises scattering the aqueous solution to the cement hardened body.

<5>

The method according to <1>, in which, an equivalent amount of fixed carbon dioxide per 1 ton of the cement hardened body on a site with carbon dioxide fixed is 30 kg or more.

<6>

The method according to <1>, including causing a potassium ion-containing aqueous solution to absorb carbon dioxide gas to obtain a potassium carbonate aqueous solution, in which an operation of the carbon dioxide gas absorption step is performed prior to the carbonate supplying step.

<7>

A carbon dioxide-fixed cement hardened body including carbon

dioxide, in which the carbon dioxide is wholly or partially fixed using the method according to any one of <1> to <6>.

<8>

A carbon dioxide-fixed cement hardened body production method, including fixing carbon dioxide to the whole or a part of the cement hardened body using the carbon dioxide fixation method according to any one of <1> to <6>.

Effects of the Invention

[0010]

The present invention makes it possible to provide a carbon dioxide fixation method capable of efficiently fixing carbon dioxide to a cement hardened body, a carbon dioxide-fixed cement hardened body to which carbon dioxide is fixed by the fixation method, and a production method therefor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

FIG. 1 is a graph illustrating results of Example 1 and Comparative Example 1;

FIG. 2 is a graph illustrating a result of Example 2; and

FIG. 3 is a graph illustrating a result of Example 3.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0012]

The carbon dioxide fixation method according to carbon dioxide gas supplying step, in which an aqueous solution (hereinafter referred to as "feed solution") of at least one

carbonate selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, and potassium bicarbonate is supplied to a cement hardened body. Furthermore, the method for producing the carbon dioxide-fixed cement hardened body according to this embodiment includes fixing carbon dioxide to the whole or a part of the cement hardened body using the carbon dioxide fixation method according to this embodiment. The carbon dioxide fixation method and the carbon dioxide-fixed cement hardened body production method according to an embodiment of the present invention will be collectively explained below.

[0013]

[Carbonate Supplying Step]

(Cement Hardened Body)

The cement hardened body for use in this embodiment is an object targeted for the carbon dioxide fixation, and may be used without particular restriction as long as it is a hardened cement. Specific examples of the cement hardened body for use in this embodiment include a hardened cement paste or mortar, concrete, a recycled aggregate, and a concrete sludge.

[0014]

In this embodiment, the cement hardened body may be in any shape, such as powder, particle, block, rod, plate, lump, wall, or decorative shapes, and may be in a regular shape or an irregular shape. Furthermore, the cement hardened body may be a part of some object, structure, or the like and may be a movable object or an immovable object.

[0015]

(Feed Solution)

In this embodiment, the feed solution to be supplied to the cement hardened body is a sodium carbonate aqueous solution, a sodium bicarbonate aqueous solution, a potassium carbonate aqueous solution, a potassium bicarbonate aqueous solution, or an aqueous solution containing two or more of these carbonates mixed. Since ions of these alkali metals (sodium, potassium) can take in a large amount of carbon dioxide gas (carbon dioxide), the ions can efficiently contribute to carbon dioxide fixation.

[0016]

Among these alkali metals, potassium can take in more carbon dioxide gas. Thus, the feed solution is preferably an aqueous solution containing potassium carbonate or potassium bicarbonate, more preferably an aqueous solution containing potassium carbonate, even more preferably a potassium carbonate aqueous solution. The potassium carbonate aqueous solution exhibits a high alkalinity of pH 11 or higher even at a low concentration, and therefore, also in this regard, the potassium carbonate aqueous solution is preferable for the feed solution that should be maintained at a high alkalinity, as described later.

[0017]

For improving the efficiency of the carbon dioxide fixation, the concentration of the alkali metal carbonate (including alkali metal bicarbonates; the same applies to the

followings regarding "alkali metal carbonate") in the feed solution is preferably high, specifically, preferably 1 mass% or higher, more preferably 5 mass% or higher, even more preferably 10 mass% or higher.

If the cement hardened body to be supplied (brought into contact with the solution) is wet or contains water, the concentration of the alkali metal carbonate in the feed solution should be adjusted in consideration of the water content.

[0018]

Since potassium carbonate has a higher water solubility compared to sodium carbonate, the potassium carbonate concentration can be increased. The potassium carbonate concentration in the feed solution is preferably 15 mass% or higher, more preferably 20 mass% or higher, even more preferably 25 mass% or higher.

[0019]

In this embodiment, the feed solution can be prepared without particular restriction, and may be obtained as an industrial product or by-product, or acquired from an outside supplier such as another company and another facility. Also, potassium carbonate contained in plant ash, biomass ash, or the like may be dissolved in water to obtain a feed solution containing predetermined carbonate ions and potassium ions. Alternatively, the feed solution may be obtained by the operation of the carbon dioxide gas absorption step described later.

[0020]

(Supplying of Feed Solution to Cement Hardened Body)

In the carbonate supplying step, the method of supplying the feed solution to the cement hardened body is not particularly limited as long as the feed solution can be brought into contact with the cement hardened body. Specific examples of the method include a method of immersing the cement hardened body in the feed solution, a method of scattering the feed solution to the cement hardened body, or a method of causing the feed solution to permeate the cement hardened body.

[0021]

When the cement hardened body is small-sized, the method of immersing the cement hardened body in the feed solution is preferable because carbon dioxide can be efficiently fixed by impregnating the cement hardened body with the feed solution from the entire surface of the cement hardened body. On the other hand, when the cement hardened body is large-sized, or is a part of some object or structure, or is an immobile object, the method of scattering the feed solution to the cement hardened body is preferable. Examples of the method of scattering the feed solution to the cement hardened body include, but are not particularly limited to, a method of pouring the feed solution using a hose or the like, and a method of squirting the feed solution in a shower form or mist form using spray, atomizer, or the like.

[0022]

When the feed solution is supplied to the cement hardened

body, the impregnation may be enhanced by pressurization/depressurization or the like to efficiently impregnate the cement hardened body with the feed solution.

[0023]

The pH of the feed solution supplied in this embodiment is preferably 9 or higher, more preferably 11 or higher and 14 or lower. Since the pH of the feed solution supplied in this embodiment is high, a crystalline basic calcium carbonate or calcium carbonate is produced after a stage in which amorphous calcium carbonate is once produced. Furthermore, the high pH of the feed solution makes it possible to maintain fixed carbon dioxide in the form of carbonate ions and suppress acid deterioration.

[0024]

By supplying the feed solution to the cement hardened body (wetting), amorphous calcium carbonate and basic calcium carbonate are efficiently produced, so that carbon dioxide is efficiently fixed. Amorphous calcium carbonate and basic calcium carbonate are produced by the reaction between calcium ions originally contained in the cement hardened body and carbonate ions contained in the feed solution, and therefore carbonate ions in the feed solution can be consumed to stably fix carbon dioxide into the cement hardened body.

[0025]

Since the fixation of carbon dioxide by supplying the feed solution to the cement hardened body (wetting) is efficient and rapidly proceeds, the time required for the

fixation (curing time, curing days) can be shortened. Depending on the method for supplying the feed solution (wetting method), the fixation reaction can be proceeded even in a curing time of about 24 hours. Thus, the curing time can be set to a duration shorter than 24 hours, e.g., 18 hours, 12 hours, 8 hours, or 4 hours. Since the fixation with carbon dioxide gas requires several days or more until the fixation reaction proceeds to some extent, the curing time (curing days) can be significantly shortened according to this embodiment (fixation by the feed solution).

[0026]

The temperature of the feed solution during supplying it to the cement hardened body may be room temperature (e.g., 20°C to 30°C) without particular restriction. A lower temperature is also acceptable, but an excessively low temperature deteriorates the reactivity, and therefore the temperature is preferably 5°C or higher, more preferably 10°C or higher. For example, when the feed solution contains a high concentration of alkali metal carbonate at a high temperature, the feed solution is supplied to (brought into contact with) the cement hardened body while maintaining a temperature at which the concentration is kept, and then the temperature may be maintained, or the cement hardened body may be left in the course of nature.

[0027]

Furthermore, the ambient temperature during the supplying of the feed solution to the cement hardened body may be room

temperature (e.g., 20°C to 30°C) without particular restriction. In the method of immersing the cement hardened body in the feed solution, the temperature is hardly affected by ambient temperature, but in the method of scattering the feed solution to the cement hardened body, the temperature of the feed solution is affected by ambient temperature after the scattering. Thus, when it is intended to maintain the temperature of the feed solution, it is preferable that the temperature of the feed solution and the ambient temperature are maintained at a same level or close levels (e.g., their difference is within $\pm 10^{\circ}\text{C}$, preferably within $\pm 5^{\circ}\text{C}$).

[0028]

[Carbon Dioxide Gas Absorption Step]

The carbon dioxide fixation method according to this embodiment may include causing a potassium ion-containing aqueous solution to absorb carbon dioxide gas to obtain a potassium carbonate aqueous solution.

[0029]

The operation of this carbon dioxide gas absorption step is performed prior to the carbonate supplying step. Then, the potassium carbonate aqueous solution obtained in the carbon dioxide gas absorption step is used as the feed solution in the subsequent carbonate supplying step.

[0030]

Examples of the aqueous solution which contains potassium ion include Potassium hydroxide • potassium carbonate potassium bicarbonate aqueous solution.

[0031]

The operation of the carbon dioxide gas absorption step can be applied to this embodiment using, as the operation of the carbon dioxide gas absorption step, a part of the operation known as the so-called "chemical absorption method" for separating and recovering carbon dioxide from other components, by absorbing carbon dioxide contained in exhaust gas with a high carbon dioxide concentration into an alkaline solution as a carbon dioxide separation and recovery technology.

[0032]

In particular, a hot potassium carbonate absorption method of absorbing carbon dioxide into a potassium carbonate aqueous solution can be suitably used as the operation of the carbon dioxide gas absorption step. Examples of the hot potassium carbonate absorption method include Benfield method and Catacarb® method. The operations and conditions of the carbon dioxide gas absorption step are conventionally known, and the known processes and conditions should also be applied to this embodiment.

[0033]

The operation of the carbon dioxide gas absorption step can be easily performed in a closed space. The subsequent carbonate supplying step can also be performed in a closed space. Even if the operation of the carbonate supplying step is performed in an open space, the risk of carbon dioxide being released in a form of carbon dioxide gas is low because

carbon dioxide is contained in the feed solution. Thus, in the carbon dioxide fixation method according to this embodiment, the risk of carbon dioxide gas being released is low throughout the whole process including the carbon dioxide gas absorption step. In contrast, the carbon dioxide fixation with carbon dioxide gas cannot be easily performed in a closed space.

[0034]

[Carbon Dioxide-Fixed Cement Hardened Body]

The carbon dioxide-fixed cement hardened body can be efficiently produced through a step in which carbon dioxide is wholly or partially fixed to the hardened body by the carbon dioxide fixation method according to the above embodiment. It produced in this manner can be used as a construction member. Carbon dioxide can be semi-permanently fixed by utilizing as construction members, objects or structures to which carbon dioxide is fixed. In this embodiment, "construction member" means a part or the whole of an architectural or civil engineering structure, or a construction material (architectural material and civil engineering material) used for architectural or civil engineering structures.

[0035]

When hardened bodies formed from cement paste, mortar, and concrete are used as the cement hardened bodies, the hardened bodies can be used as a construction member composed of these hardened bodies or partially containing these hardened bodies, and is environmentally friendly because

carbon dioxide can be fixed to the construction member. When using a recycled aggregate as the cement hardened body, the cement hardened body itself can be used as an aggregate (construction material) that is a recycled product having an excellent resource-saving property. Since carbon dioxide can be fixed to this aggregate, the recycled aggregate is environment friendly, synergistically with the resource-saving property.

[0036]

Furthermore, when using a concrete sludge as the cement hardened body, it can be reused as a concrete material such as fine aggregate and coarse aggregate or as a recycled roadbed material (these are referred to as construction materials). Since carbon dioxide can be fixed to the concrete material and the recycled roadbed material, the concrete sludge is environmentally friendly.

[0037]

In the carbon dioxide fixation method according to this embodiment, carbon dioxide can be efficiently fixed to the cement hardened body, and therefore, when using this cement hardened body as an architectural member, a large amount of carbon dioxide can be fixed to it. For example, a construction member with fixed carbon dioxide in an equivalent amount of 30 kg or more per 1 ton of the cement hardened body, which has not been easy to fix so far, can be provided to a site with fixed carbon dioxide.

[0038]

The "carbon dioxide equivalent amount" refers to an amount equivalent to the CO₂ amount in the total amount of carbonate fixed in a form of CaCO₃, which is generally denoted as "fixed CO₂ amount". The fixed CO₂ amount can be measured, for example, by a method implemented in Examples described later.

[0039]

The embodiments described above merely illustrate representative aspects of the present invention, and the present invention is not limited to the embodiments. That is, those skilled in the art can variously modify the present invention within the scope not departing from the gist of the present invention, according to conventionally known knowledge. As long as this modification still possesses the carbon dioxide fixation method and the composition of the construction member to which carbon dioxide is fixed by the method according to the present invention, the modification is obviously included in the scope of the present invention.

EXAMPLES

[0040]

The present invention will be explained below with reference to Examples, but the present invention is not limited to the following Examples. Note that the operations of Example 1 in [Test 1] and Example 2 in [Test 2] were performed in parallel.

[0041]

[Test 1]

<Example 1>

(1) Preparation of Sample A (Cement Hardened Body)

A recycled fine aggregate L (conforming product, in accordance with JIS A 5023 Appendix A) was prepared, which is a recycled material stuck with a cement hardened body targeted for the carbon dioxide fixation.

[0042]

In measurements in accordance with "JIS A 1109: Test Methods for Density and Water Absorption Rate of Fine Aggregate" prior to the test, the fine aggregate had an apparent density of 2.23 g/cm³, an absolute dry density was 1.99 g/cm³, a water absorption rate of 12.50% (JIS A 5023 Recycled Fine Aggregate L Standard Value: 13.0% or less), a fine particle content of 3.4% (JIS A 5023 Recycled Fine Aggregate L Standard Value: 10.0% or less), and a particle size of 5 mm or less.

[0043]

Sample A of the prepared recycled fine aggregate L was maintained in an air-dried state. Some samples were collected and subjected to a measurement of the (pre-test) CO₂ content described later. The residue of Sample A was subjected to sample reduction, to uniformly collect 10 samples in an amount of 100 g or more (required amount per 1 test) (five curing time benchmarks, n=2).

[0044]

(2) Preparation of Feed Solution A (Potassium Carbonate

Aqueous Solution)

To 100 mL of water, 30 g of potassium carbonate was added and dissolved by thoroughly stirring the mixture to prepare a 23 mass% potassium carbonate aqueous solution as the feed solution A.

[0045]

(3) Supplying of Feed Solution A to Sample A (Carbonate Supplying Step)

Under a condition of 20°C and 60% RH, about 100 g of Sample A was immersed in 400 g or more of the feed solution A (20°C) and left to stand. Regarding the curing (standing) time, five benchmarks: 3 hours, 9 hours, 15 hours, 24 hours (1 day), and 72 hours (3 days) were set, with n=2 for each test. After the curing time elapsed, the feed solution A was removed using a pipette or the like, and Sample A was taken out.

[0046]

(4) Drying of Sample A

The collected Sample A was immersed in acetone and left to stand for 6 hours or longer to remove free water. Subsequently, Sample A was evacuated in a vacuum drying oven for 6 hours or longer until it became an absolute dry state.

[0047]

(5) Post-Treatment of Sample A

Sample A in the absolute dry state was ground using a ball mill while performing sample reduction as appropriate until its size became about 100 μm , and then vacuum-dried to prepare an analytical test sample. Sample A was stored in a

desiccator before the analytical test.

[0048]

<Comparative Example 1>

(1) Preparation of Sample B (Cement Hardened Body)

In the same manner as in "(1) Preparation of Sample A (Cement Hardened Body)" in Example 1, Sample B for Comparative Example 1 was prepared (including measurements of water content and CO₂ content). However, the number of the collected samples was 6 (three curing time benchmarks, n=2).

[0049]

(2) Supplying of Carbon Dioxide Gas to Sample B (Carbonation Curing)

Sample B was evenly spread in a tray having a suitable size, the tray was allowed to stand in a carbonation curing tank, and carbonation curing was initiated. In the carbonation curing tank, the curing was performed under a condition of 17% CO₂ concentration, 20°C, and 60% RH. Regarding the curing (standing) time, three benchmarks: 24 hours (1 day), 48 hours (2 days), and 72 hours (3 days) were set, with n=2 for each test. After the curing time elapsed, Sample B was taken out from the carbonation curing tank and subjected to sample reduction as appropriate. At this time, a part of the sample was collected and subjected to a measurement of the water content after the curing.

[0050]

(3) Post-Curing Treatment

In the same manner as in "(4) Drying of Sample A" and

"(5) Post-Treatment of Sample A" in Example 1, Sample B was dried, post-treated, and stored in a desiccator.

[0051]

<Measurement of Fixed CO₂ Amount>

For Sample A and Sample B obtained after each test in Example 1 and Comparative Example 1, their (post-test) CO₂ contents were measured. The CO₂ contents, including the (pre-test) CO₂ contents measured before each test in Example 1 and Comparative Example 1, were determined using a "wet analysis method". In the wet analysis method, the sample is decomposed with hydrochloric acid to produce carbon dioxide, then carbon dioxide is introduced and absorbed into a solution of barium chloride and sodium hydroxide, and CO₂ content was measured by titration with a standard hydrochloric acid solution.

[0052]

From the determined (pre-test) CO₂ content and (post-test) CO₂ content measurement results, a fixed CO₂ amount was calculated according to Equation (1) below.

[0053]

[Equation 1]

$$CO_{2\text{Fix}} = \left(CO_2' \times \frac{(1 - CO_2)}{(1 - CO_2')} - CO_2 \right) \times 100 \quad (1)$$

[0054]

Each term in Equation (1) above is defined as follows.

CO_{2Fix}: fixed CO₂ amount [kg/t]

CO₂': (pre-test) CO₂ content [%]

CO₂: (post-test) CO₂ content [%]

[0055]

For each of the curing times in Example 1 and Comparative Example 1, tests were conducted with n=2, and therefore the average of the two measurement values was taken as the fixed CO₂ amount. The results of the determined fixed CO₂ amounts are as illustrated in Table 1 below and a graph in FIG. 1.

[0056]

[Table 1]

Curing time (h)	Example 1: Potassium carbonate aqueous solution (23% concentration)	Comparative Example 1: CO ₂ gas (17% concentration)
0	0.0	0
3	20.7	-
9	25.4	-
15	26.9	-
24	34.5	16.3
48	-	26.3
72	38.2	27.3

* The values in the table are fixed CO₂ amounts (kg/t).

[0057]

<Discussion for Results of Example 1 and Comparative Example 1>

As can be seen from the above Table 1 and the graph in FIG. 1, the fixed CO₂ amount in Comparative Example 1 (CO₂ gas (17% concentration)) is 16.3 kg/t in the curing time of 24 hours and 27.3 kg/t in the curing time of 72 hours, and in contrast, the fixed CO₂ amount in Example 1 (immersion in potassium carbonate aqueous solution (23% concentration)) is 34.5 kg/t in the curing time of 24 hours and 38.2 kg/t in the

curing time of 72 hours, indicating that the CO₂ fixation efficiency of the potassium carbonate aqueous solution is significantly high.

[0058]

In Example 1, the fixed CO₂ amount is 20.7 kg/t even in the short curing time of 3 hours, which is greater than that in Comparative Example 1 with the curing time of 24 hours. This result indicates that, while the fixation reaction with CO₂ gas proceeds gradually, the fixation reaction with the potassium carbonate aqueous solution rapidly proceeds within a short period.

[0059]

In Example 1, X-ray diffraction results indicated that CO₂ was fixed and present in a form of calcium carbonate that was a stable phase, in samples of all curing times. Also in Comparative Example 1, X-ray diffraction results indicated production of calcium carbonate. Thus, it was confirmed that, in both Example 1 and Comparative Example 1, CO₂ was fixed owing to production of calcium carbonate in the cement hardened body, similarly to the conventional neutralization/carbonation reactions.

[0060]

[Test 2]

<Example 2>

(1) Preparation of Sample C (Cement Hardened Body)

In the same manner as in "(1) Preparation of Sample A (Cement Hardened Body)" in Example 1, Sample C for Example 2 was

prepared (including measurements of water content and CO₂ content). However, the number of the collected samples was 6 (three potassium carbonate concentration benchmarks, n=2).

[0061]

(2) Preparation of Feed Solutions B to D (Potassium Carbonate Aqueous Solutions)

Potassium carbonate was added to water, varying the proportion of potassium carbonate to water such that the potassium carbonate concentrations were 30 mass%, 40 mass%, and 53 mass%. The mixture was thoroughly stirred to dissolve potassium carbonate, to prepare three types of potassium carbonate aqueous solutions: feed solution B (30 mass%), feed solution C (40 mass%), and feed solution D (53 mass%). Note that 53 mass% potassium carbonate concentration corresponds to the saturated one.

[0062]

(3) Supplying of Feed Solutions B to D to Sample C (Carbonate Supplying Step)

Under a condition of 20°C and 60% RH, about 100 g of sample C was immersed in each of the feed solutions B to D (20°C) in an amount of 400 g or more, and left to stand. The curing (standing) time was set to 24 hours (1 day), with n=2 for the test. After the curing time elapsed, each of the feed solutions B to D was removed using a pipette or the like, and Sample C was taken out. Hereafter, Sample C immersed in the feed solution B is denoted as Sample CB, Sample C immersed in the feed solution C is denoted as Sample CC, and Sample C

immersed in the feed solution D is denoted as Sample CD.

[0063]

(4) Post-Curing Treatment

In the same manner as in "(4) Drying of Sample A" and "(5) Post-Treatment of Sample A" in Example 1, Sample CB, Sample CC, and Sample CD were each dried, post-treated, and stored in a desiccator.

[0064]

<Measurement of Fixed CO₂ Amount>

For Sample CB, Sample CC, and Sample CD obtained after each test in Example 2, the (post-test) CO₂ content was measured in the same manner as in Example 1. From the determined measurement results of the (pre-test) CO₂ content and the (post-test) CO₂ content, the fixed CO₂ amount was calculated in the same manner as in Example 1.

[0065]

For each potassium carbonate concentration in Example 2, tests were conducted with n=2, and therefore the average of the two measurement values was taken as the fixed CO₂ amount. The results of the determined fixed CO₂ amounts are as illustrated in Table 2 below and a graph in FIG. 2. Note that Table 2 and FIG. 2 also include the results of the 24-hour curing time in Example 1 as data of the 23% potassium carbonate concentration.

[0066]

[Table 2]

Sample	Potassium carbonate concentration(%)	Fixed CO ₂ amount (kg/t)
-	0	0
Sample A (24h)	23	34.55
Sample CB	30	41.97
Sample CC	40	47.89
Sample CD	53	77.02

* The values in the table are fixed CO₂ amounts (kg/t).

[0067]

<Discussion for Results of Example 2>

As can be seen from the graph in the above Table 2 and the graph in FIG. 2, the higher the potassium carbonate concentration in the feed solution is, the higher the CO₂ fixation efficiency is, and the CO₂ fixation efficiency is highest at a potassium carbonate concentration of 53 mass%, which is a saturated potassium carbonate concentration in the aqueous solution.

[0068]

In Example 2, the X-ray diffraction results indicated that, in any samples with any potassium carbonate concentration, CO₂ was fixed and present in a form of calcite (calcium carbonate) as a stable phase.

[0069]

[Test 3]

<Example 3>

(1) Preparation of Sample D (Cement Hardened Body)

A sludge cake was prepared from a concrete sludge extracted from a washing waste liquid of a concrete mixer truck. After dehydration pressing, the prepared sludge cake

had a water content of 45.1% and a CaO content of 66.5%.

[0070]

The sludge cake was crushed into pieces with sizes of 10 mm or smaller by using a jaw crusher. Particle size adjustment was performed by sieving to obtain a sand-like concrete sludge with particle sizes of 1.2 to 5 mm. The obtained concrete sludge was immersed in acetone and left to stand for 6 hours or longer to remove free water. Subsequently, the concrete sludge was evacuated in a vacuum drying oven for 6 hours or longer until it became an absolute dry state, to prepare Sample D that is a concrete sludge as the cement hardened body targeted for the carbon dioxide fixation.

[0071]

From the prepared Sample D, some samples were collected and subjected to a (pre-test) CO₂ content measurement in the same manner as in Example 1. The residue of Sample D was subjected to sample reduction, to uniformly collect 8 samples in an amount of about 200 g (required amount per 1 test, depending on a collectable sample amount) (two K₂CO₃ concentration benchmarks, two curing time benchmarks, n=2).

[0072]

(2) Preparation of Feed Solution E to G (Potassium Carbonate Aqueous Solution)

Potassium carbonate was added to water, varying the proportion of potassium carbonate to water such that the potassium carbonate concentrations were 15 mass%, 27 mass%, and 53 mass%. The mixture was thoroughly stirred to dissolve

potassium carbonate, to prepare three types of potassium carbonate aqueous solutions: feed solution E (15 mass%), feed solution F (27 mass%), and feed solution G (53 mass%).

[0073]

The feed solution G obtained herein is the same as the feed solution D obtained in Example 2 and has a potassium carbonate concentration corresponding to the saturated potassium carbonate concentration in the aqueous solution. In the feed solution F, the 27 mass% potassium carbonate concentration in the aqueous solution was set by referring to, as a measure, an amount corresponding to the calcium amount in the concrete sludge. In the feed solution E, the 15 mass% potassium carbonate concentration was set by referring to, as a measure, half of an amount corresponding to the calcium amount in the concrete sludge.

[0074]

(3) Supplying of Feed Solutions E to G to Sample D (Carbonate Supplying Step)

Under a condition of 20°C and 60% RH, about 200 g of Sample D was immersed in 1000 g or more of each of the feed solutions E to G (20°C) and left to stand. Regarding the curing (standing) time, two benchmarks: 1 day and 3 days were set, with n=2 for each test. After the curing time elapsed, each of the feed solutions E to G was removed using a pipette or the like, and Sample D was taken out. Hereafter, Sample D immersed in the feed solution E is denoted as Sample DE, Sample D immersed in the feed solution F is denoted as Sample

DF, and Sample D immersed in the feed solution G is denoted as Sample DG.

[0075]

(4) Post-Curing Treatment

In the same manner as in "(4) Drying of Sample A" and "(5) Post-Treatment of Sample A" in Example 1, Sample DE, Sample DF, and Sample DG were each dried, post-treated, and stored in a desiccator.

[0076]

<Measurement of Fixed CO₂ Amount>

For Sample DE, Sample DF, and Sample DG obtained after each test in Example 3, the (post-test) CO₂ content was measured in the same manner as in Example 1. From the determined measurement results of the (pre-test) CO₂ content and the (post-test) CO₂ content, the fixed CO₂ amount was calculated in the same manner as in Example 1.

[0077]

For each potassium carbonate concentration and each curing time in Example 3, tests were conducted with n=2, and therefore the average of the two measurement values was taken as the fixed CO₂ amount. The results of the determined fixed CO₂ amounts are as illustrated in Table 3 below and a graph in FIG. 3.

[0078]

[Table 3]

Sample	Sample DE	Sample DF	Sample DG
Curing days (d)	Potassium carbonate aqueous solution (15% concentration)	Potassium carbonate aqueous solution (27% concentration)	Potassium carbonate aqueous solution (53% concentration)
0	0	0	0
1	117.97	120.87	119.60
3	145.16	136.60	165.99

* The values in the table are fixed CO₂ amounts (kg/t).

[0079]

<Discussion for Results of Example 3>

As can be seen from the above Table 3 and the graph in FIG. 3, carbon dioxide in an amount as large as about 120 g/t could be fixed even in a short curing time (1 day) in all potassium carbonate concentrations. This may be because the concrete sludge as the cement hardened body is porous with a large specific surface area and furthermore has a high calcium content originated from a cement hydrate such as calcium hydroxide, and therefore carbon dioxide could be sufficiently and efficiently fixed even in a short curing time. When the curing time is extended to 3 days, the higher the potassium carbonate concentration is, the more the carbon dioxide can be fixed. However, in the case of extended curing time, the fixation efficiency decreases compared to that of the initial curing time.

[0080]

In Example 3, the X-ray diffraction results indicated that, in any samples with any potassium carbonate concentration or any curing time, CO₂ was fixed and present in a form of calcite (calcium carbonate) as a stable phase.

CLAIMS

[Claim 1]

A method for fixing carbon dioxide to a cement hardened body, comprising:

supplying an aqueous solution of at least one carbonate selected from the group consisting of sodium carbonate, sodium bicarbonate, potassium carbonate, and potassium bicarbonate to the cement hardened body.

[Claim 2]

The method according to claim 1, wherein the aqueous solution contains potassium carbonate, and a potassium carbonate concentration in the aqueous solution is 15 mass% or higher.

[Claim 3]

The method according to claim 1, wherein the method of supplying the aqueous solution to the cement hardened body comprises immersing the cement hardened body in the aqueous solution.

[Claim 4]

The method according to claim 1, wherein the method of supplying the aqueous solution to the cement hardened body comprises scattering the aqueous solution to the cement hardened body.

[Claim 5]

The method according to claim 1, wherein an equivalent amount of fixed carbon dioxide per 1 ton of the cement hardened body on a site with carbon dioxide fixed is 30 kg or more.

[Claim 6]

The method according to claim 1, comprising:

causing a potassium ion-containing aqueous solution to absorb carbon dioxide gas to obtain a potassium carbonate aqueous solution,

wherein an operation of the carbon dioxide gas absorption step is performed prior to the carbonate supplying step.

[Claim 7]

A carbon dioxide-fixed cement hardened body,
comprising carbon dioxide,

wherein the carbon dioxide is wholly or partially fixed using the method according to any one of claims 1 to 6.

[Claim 8]

A carbon dioxide-fixed cement hardened body production method, comprising:

fixing carbon dioxide to the whole or a part of the cement hardened body using the method according to any one of claims 1 to 6.