DESCRIPTION

CO_2-IMMOBILIZING EXPANSIVE MATERIAL, CEMENT COMPOSITION, AND CONCRETE COMPOSITION

Technical Field

[0001]

The present invention relates to a CO_2-immobilizing expansive material, a cement composition, and a concrete composition.

Background Art

[0002]

Reduction of cracks in cement and concrete is important from the viewpoint of reliability, durability, aesthetics, and the like of products and structures. Therefore, further development of a technique of an expansive material having an effect of improving these is desired.

[0003]

In addition, in order to reduce the total amount of CO_2 discharged when a concrete product is produced, it is effective to reduce the amount of cement used by blending a large amount of special admixture or industrial by-product (ground granulated blast furnace slag, fly ash, or the like) as a substitute for cement, and various studies have been conducted.

[0004]

Under such circumstances, a technique for absorbing (immobilizing) CO_2 in a cement hardened body has also been studied. For example, Patent Literature 1 discloses a method for forcibly absorbing or carbonating CO_2 during production. Specifically, a method for immobilizing carbon dioxide is disclosed, the method including a contact step of bringing a carbon dioxide-containing gas into contact with a cementitious hardened body to immobilize carbon dioxide contained in the carbon dioxide-containing gas in the cementitious hardened body.

Citation List

Patent Literature

[0005]

Patent Literature 1: JP 2020-15659 A

Summary of Invention

Technical Problem

[0006]

However, in the immobilization method of Patent Literature 1, the amount of water in the carbon dioxide-containing gas is set to 1.5% or more and the temperature is set to 75 to 175°C, but there is no disclosure or suggestion about a material that immobilizes CO_2. In

addition, there is no disclosure of an expansive material.

[0007]

From the above, an object of the present invention is to provide a CO_2-immobilizing expansive material having good expansion performance and CO_2-immobilizing performance.

Solution to Problem

[0008]

As a result of intensive studies to solve the above problems, the present inventors have conceived the following present invention and found that the problems can be solved. That is, the present invention is as follows.

[0009]

[1] A CO_2-immobilizing expansive material containing an ettringite-generating compound that generates ettringite.

[2] The CO_2-immobilizing expansive material according to [1], wherein the ettringite-generating compound contains free lime as a mineral composition.

[3] The CO_2-immobilizing expansive material according to [2], containing 10 to 70 mass% of the free lime.

[4] The CO_2-immobilizing expansive material according to any one of [1] to [3], wherein the ettringite-

generating compound contains hauyne as a mineral composition.

[5] The CO_2-immobilizing expansive material according to any one of [1] to [4], wherein the ettringite-generating compound contains ternesite and/or gehlenite as a mineral composition.

[6] The CO_2-immobilizing expansive material according to [5], wherein a content (total content) of the ternesite and the gehlenite in the ettringite-generating compound is 2 to 15 mass%.

[7] The CO_2-immobilizing expansive material according to any one of [1] to [6], wherein a Blaine specific surface area is 2000 to 6000 cm^2/g.

[8] The CO_2-immobilizing expansive material according to any one of [1] to [7], for use mixed with cement.

[9] A cement composition containing the CO_2-immobilizing expansive material according to any one of [1] to [8] and cement.

[10] A concrete composition containing the CO_2-immobilizing expansive material according to any one of [1] to [8], cement, and an aggregate.

Advantageous Effects of Invention

[0010]

According to the present invention, it is possible to provide a CO_2-immobilizing expansive material having good expansion performance and CO_2-immobilizing performance.

Description of Embodiments

[0011]

Hereinafter, an embodiment of the present invention (the present embodiment) will be described in detail.

[0012]

[CO_2-immobilizing expansive material]

The CO_2-immobilizing expansive material of the present embodiment contains an ettringite-generating compound that generates ettringite. In the present embodiment, in a cement composition or a concrete composition containing the CO_2-immobilizing expansive material, ettringite generated along with solidification of the cement composition or the concrete composition incorporates carbon dioxide (CO_2) into its crystal, thereby absorbing CO_2. In addition, due to expansion performance of the CO_2-immobilizing expansive material, a good expansion effect is exhibited.

Here, the “solidification” refers to a state in which compressive strength is 2.5 N/mm^2 or more in accordance with a method specified in JIS R 5201:2015

“Physical testing methods for cement”.

[0013]

Regarding the CO_2 absorption described above, it is expected that a large amount (generated ettringite is expected to absorb 3 moles, 4.2 moles, or 4.6 moles of CO_2 per mole of ettringite) of CO_2 is absorbed by the generated ettringite according to any one of the following formulas (1) to (3) although the absorption depends on conditions such as humidity.

Formula (1): $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \rightarrow 3CaCO_3 + Al_2O_3$ (gel) $+ 3CaSO_4 \cdot 2H_2O + 26H_2O$

Formula (2): $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31.1H_2O + 4.6CO_2 \rightarrow 3CaCO_3 + Al_2O_3 \cdot 10.4H_2O \cdot 1.6CO_2 + 3CaSO_4 \cdot 0.5H_2O + 19.2H_2O$

Formula (3): $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30.9H_2O + 4.2CO_2 \rightarrow 3CaCO_3 + Al_2O_3 \cdot 7.9H_2O \cdot 1.2CO_2 + 3CaSO_4 \cdot 2H_2O + 17.0H_2O$

[0014]

The ettringite-generating compound according to the present embodiment is not particularly limited as long as the ettringite-generating compound is a compound that generates ettringite, and examples thereof include at least one or more selected from the group consisting of calcium sulfoaluminate, calcium aluminate, calcium fluoroaluminate, calcium chloroaluminate, alinite, $Na_2O \cdot 8CaO \cdot 3Al_2O_3$, alum, sulfate, and the like.

Among them, a combination of at least one of calcium

sulfoaluminate and calcium aluminate and a sulfate is preferable from the viewpoint of development of good strength and CO_2 immobilization amount.

[0015]

Here, the calcium aluminate (CA) according to the present embodiment is a generic term for compounds containing CaO and Al_2O_3 as main components, and specific examples thereof include amorphous compounds containing a CaO component and an Al_2O_3 component as main components, and crystalline calcium aluminates represented by $CaO \cdot 2Al_2O_3$, $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $11CaO \cdot 7Al_2O_3 \cdot CaF_2$, and $3CaO \cdot 3Al_2O_3 \cdot CaF_2$.

Among them, the CaO/Al_2O_3 molar ratio of CA is preferably in a range of 0.45 to 3, and more preferably in a range of 0.8 to 2. When the CaO/Al_2O_3 molar ratio is 0.45 or more, sufficient initial strength development is obtained. In addition, when the CaO/Al_2O_3 molar ratio is 3 or less, sufficient flowability and pot life are obtained.

[0016]

As described above, calcium aluminate in either crystalline or amorphous form can be used, but amorphous calcium aluminate obtained by rapidly cooling a melt in an electric furnace or the like is preferable, and when the content of amorphous calcium aluminate is 60 mass% or more, the calcium aluminate is excellent in strength development

in a short time. The proportion of the amorphous phase (degree of amorphization) can be determined by powder X-ray diffraction/Rietveld analysis.

[0017]

The calcium sulfoaluminate (CSA) according to the present embodiment is produced by, for example, calcining a calcareous raw material such as lime, a sulfate raw material such as gypsum, and an alumina raw material such as bauxite at about 1300°C to 1600°C using a kiln or the like, and pulverizing the calcined raw material.

The CSA is not particularly limited, and examples thereof include one obtained by blending raw materials at a molar ratio of CaO : Al_2O_3 : $CaSO_4$ of 3 : 3 : 1 and calcining and pulverizing the raw materials. This is called hauyne ($3CaO \cdot 3Al_2O_3 \cdot CaSO_4$).

[0018]

From the viewpoint of an expansion rate, it is preferable that the ettringite-generating compound contains free lime as a mineral composition. In the ettringite-generating compound, 3 to 80 mass% of free lime is preferably contained, and 15 to 65 mass% of free lime is more preferably contained. By containing 3 to 80 mass% of free lime, excellent expansion performance can be secured.

[0019]

In addition, from the viewpoint of the expansion

rate and securing the strength, the ettringite-generating compound preferably contains hauyne as a mineral composition. In the ettringite-generating compound, 1 to 30 mass% of hauyne is preferably contained, and 3 to 25 mass% of hauyne is more preferably contained. By containing 1 to 30 mass% of hauyne, both excellent expansion performance and strength development can be achieved.

[0020]

From the viewpoint of efficient CO_2 immobilization, it is preferable that the ettringite-generating compound contains ternesite and/or gehlenite as a mineral composition. The total amount of ternesite and gehlenite in the ettringite-generating compound is preferably 2 to 15 mass%, and more preferably 3 to 10 mass%. By containing 2 to 15 mass% of the total amount of ternesite and gehlenite, CO_2 can be more efficiently immobilized. In order to achieve the above contents of ternesite, adjustment may be performed by, for example, mixing silicon dioxide as a reagent with the raw material.

[0021]

Examples of the sulfate include alkali metal sulfate and alkaline earth metal sulfate.

Examples of the alkali metal of the alkali metal sulfate include lithium, sodium, and potassium, and sodium

is preferable. The alkali metal sulfate may be used singly or in combination of two or more kinds.

[0022]

Examples of the alkaline earth metal of the alkaline earth metal sulfate include magnesium and calcium, and calcium is preferable. The alkaline earth metal sulfate may be used singly or in combination of two or more kinds. The particle size and grain size of the alkaline earth metal sulfate are not particularly limited, and those having a Blaine specific surface area of about 4000 to 8500 cm^2/g are exemplified.

Here, the alkaline earth metal sulfate is preferably calcium sulfate, and examples thereof include anhydrous gypsum (anhydrous calcium sulfate), hemihydrate gypsum (calcium sulfate hemihydrate), and dihydrate gypsum (calcium sulfate dihydrate). Among them, anhydrous gypsum is preferable.

[0023]

The content of the sulfate is preferably 7 to 60 parts by mass, more preferably 15 to 58 parts by mass, and still more preferably 20 to 57 parts by mass on an anhydrous basis with respect to 100 parts by mass of calcium sulfoaluminate.

In addition, the content of the sulfate is preferably 40 to 160 parts by mass, more preferably 42 to

157 parts by mass, and still more preferably 45 to 155 parts by mass on an anhydrous basis with respect to 100 parts by mass of calcium aluminate. When the content of the alkaline earth metal sulfate is within the above range, long-term strength development tends to be excellent.

[0024]

From the viewpoint of development of good strength and CO_2 immobilization amount, it is preferable that the ettringite-generating compound is calcium sulfoaluminate and/or calcium aluminate, and contains hauyne as a mineral composition. In the ettringite-generating compound, 10 mass% or more of hauyne is preferably contained, and 15 mass% or more of hauyne is more preferably contained. The amount of hauyne can be adjusted by changing the component ratio of CaO, Al_2O_3, and SO_3 in the raw material. The upper limit is not particularly limited, but is actually 80 mass%.

[0025]

In addition, from the viewpoint of development of good strength and CO_2 immobilization amount, the content of calcium sulfate as a mineral composition in the ettringite-generating compound is preferably 2 to 75 mass%, and more preferably 10 to 70 mass%.

The mineral composition of free lime, hauyne, ternesite, gehlenite, calcium sulfate, and the like in the

ettringite-generating compound can be measured by an XRD/Rietveld method.

[0026]

The Blaine specific surface area of the ettringite-generating compound is preferably 1,500 to 8,000 cm^2/g, and more preferably 2,000 to 7,000 cm^2/g from the viewpoint of sufficiently exhibiting the function.

[0027]

In the CO_2-immobilizing expansive material of the present embodiment, the Blaine specific surface area is preferably 1,500 to 8,000 cm^2/g, more preferably 2,000 to 7,000 cm^2/g, and still more preferably 2,000 to 6,000 cm^2/g from the viewpoint of sufficiently exhibiting the function.

[0028]

The content of the ettringite-generating compound is preferably 80 mass% or more, and more preferably 90 mass% or more in the CO_2-immobilizing expansive material from the viewpoint of sufficiently exhibiting the function.

[0029]

In addition, when a solidified body obtained by mixing 50 parts by mass of water with respect to 100 parts by mass of the CO_2-immobilizing expansive material and curing the mixture for 24 hours is allowed to stand for 24 hours in an environment with a CO_2 concentration of 5% at 20°C and 60%RH, the CO_2 immobilization rate is preferably

9% or more, and more preferably 10% or more.

Here, the immobilization rate can be determined by the proportion of the number of moles of reacted CaO to the number of moles of CaO before the reaction (reacted CaO-mol/CaO-mol before the reaction).

[0030]

The CO_2-immobilizing expansive material as described above can be used as it is for various applications or mixed with other materials, but in consideration of application of existing techniques related to long-term durability and maintenance at the time of using a solidified body, it is preferable that the CO_2-immobilizing expansive material is used for mixing with cement or concrete.

[0031]

[Cement composition and concrete composition]

A cement composition according to the present embodiment contains the above-described CO_2-immobilizing expansive material of the present invention and cement. In addition, a concrete composition according to the present embodiment contains the above-described CO_2-immobilizing expansive material of the present invention and cement.

The cement composition in the present embodiment is a generic term for cement, cement paste, and mortar.

[0032]

The content of the CO_2-immobilizing expansive material is preferably in a range of 5 to 90 parts by mass, and more preferably in a range of 30 to 80 parts by mass with respect to 100 parts by mass of cement from the viewpoint of improving expandability and CO_2 immobilization.

[0033]

The cement used in the present embodiment is not particularly limited, and examples thereof include various types of cements such as ordinary, early strength, ultra-early strength, low heat, and moderate heat cements, various types of mixed cements obtained by mixing blast furnace slag, fly ash, silica fume, or the like with these cements, environmentally friendly cements (eco cements) produced using urban waste incineration ash or sewage sludge incineration ash as a raw material, siliceous substances such as metakaolin and clay calcined ash, and commercially available fine-particle cements, and it is also possible to use various types of cements and various types of mixed cements after being formed into a finely powdered form. In addition, it is also possible to use those which are adjusted by increasing or decreasing the amounts of components (such as gypsum) normally used in a cement. In the present embodiment, it is preferable to select ordinary Portland cement or early strength Portland

cement from the viewpoint of hydration heat, dry shrinkage, and filling properties.

[0034]

In addition, from the viewpoint of production cost and strength development, the Blaine specific surface area of the cement is preferably 2,500 to 7,000 cm^2/g, and more preferably 2,750 to 6,000 cm^2/g.

In the present specification, the Blaine specific surface area is determined in accordance with JIS R 5201 (Physical testing methods for cement).

[0035]

Examples of the fine aggregate used in the present embodiment include river sand, mountain sand, land sand, sea sand, silica sand, crushed sand, crushed limestone sand, blast furnace slag fine aggregate, and recycled fine aggregate. The type and content of the fine aggregate may be selected according to the target mechanical strength of a concrete hardened body.

[0036]

Examples of the coarse aggregate used in the present embodiment include crushed stone obtained by crushing andesite, rhyolite, hard sandstone, limestone, and the like, river gravel, mountain gravel, land gravel, blast furnace slag coarse aggregate, and recycled coarse aggregate. The rock type, size, and content of the coarse

aggregate may be selected according to the target mechanical strength of a concrete hardened body.

[0037]

In the present embodiment, various materials may be contained. Examples thereof include a water reducing agent, an AE agent, a foaming agent, a shrinkage reducing agent, a waterproof agent, a rust inhibitor, a thickener, a polymer, a water retention agent, a pigment, a water repellent agent, and an anti-efflorescence agent.

Examples

[0038]

Hereinafter, the present invention will be described specifically with reference to examples, but the present invention is not limited thereto.

[0039]

[Experimental Example 1]

<Preparation of CO_2-immobilizing expansive material>

A calcium carbonate reagent, an aluminum hydroxide reagent, a calcium sulfate reagent, and a silicon dioxide reagent were mixed so as to have the composition shown in the following Table 1, and the mixture was heated at 1350°C for 3 hours to adjust the Blaine specific surface area to 3500 cm^2/g, thereby preparing an ettringite-generating compound, and the compound was used as a CO_2-immobilizing

expansive material.

[0040]

(Evaluation)

<Strength>

A composition having a water/powder mass ratio of 0.5 and a fine aggregate/powder mass ratio of 3.0 was molded into a specimen of 40 × 40 × 160 mm, and the strengths (JIS R 5201:2015 “Physical testing methods for cement”) at the age of 1, 3, and 7 days was measured. The ettringite-generating compound was mixed in an amount of 5% by mass with respect to the powder.

The “powder” described above refers to the total of the ettringite-generating compound and cement (ordinary Portland cement). In addition, silica sand was used as the fine aggregate. After demolding at the age of 1 day, carbonation curing was performed under conditions of a temperature of 20°C, a humidity of 60%RH, and a CO_2 concentration of 5%.

[0041]

< CO_2 absorption amount (CO_2 content rate, CO_2 immobilization rate)>

A paste having a water/powder mass ratio of 0.5 was molded into a specimen of 20 × 20 × 80 mm, and after demolding at the age of 1 day, carbonation curing was performed under conditions of a temperature of 20°C, a

humidity of 60%RH, and a CO_2 concentration of 5%. The ettringite-generating compound was mixed in an amount of 6.7% by mass with respect to the powder.

Thereafter, the test body was pulverized to 90 μm or less at a predetermined age, and then the CO_2 content was measured by a coulometer method.

The “powder” described above refers to the total of the ettringite-generating compound and cement (ordinary Portland cement).

[0042]

< Expandability >

A composition having a water/powder mass ratio of 0.5 and a fine aggregate/powder mass ratio of 3.0 was molded into a specimen of 40 × 40 × 160 mm, and the length change rate (JIS A 6202:2017 “Expansive material for concrete”) at the age of 7 and 28 days was measured. After demolding at the age of 1 day, carbonation curing was performed under conditions of a temperature of 20°C, a humidity of 60%RH, and a CO_2 concentration of 5%.

The “powder” described above refers to the total of the ettringite-generating compound and cement (ordinary Portland cement). The ettringite-generating compound was mixed in an amount of 6.7% by mass with respect to the powder. In addition, silica sand was used as the fine aggregate.

[0043]

[Table 1]

Experiment No.	Ettringite-generating compound					Evaluation								Remarks
	Mineral composition (mass%)					Strength (N/mm^2)			Expandability: length change rate ($\times 10^{-6}$)		CO_2 content rate (mass%)			
	Free lime (CaO)	$CaSO_4$	Hauyne	Ternesite + gehlenite	Total	1 day	3 days	7 days	7 days	28 days	1 day	3 days	7 days	
1-1	55	33	5	5	98	12.7	35.0	47.3	120	-100	10.8	14.4	18.8	Example
1-2	5	73	10	10	98	14.0	36.0	49.0	-100	-230	9.2	11.9	16.0	Example
1-3	30	48	10	10	98	13.0	35.8	48.2	80	-120	10.2	13.6	17.6	Example
1-4	70	8	10	10	98	11.8	34.2	45.5	300	20	11.4	15.6	19.5	Example
1-5	75	3	10	10	98	8.7	28.2	38.6	350	60	11.6	15.7	19.8	Example
1-6	20	68.5	10	1	99.5	13.6	37.2	39.8	-10	-140	9.6	10.4	15.2	Example
1-7	20	66	10	3	99	13.2	36.2	49.1	-30	-170	10.6	12.7	18.2	Example
1-8	20	56	10	13	99	12.2	33.0	45.6	-60	-190	10.3	12.1	17.9	Example
1-9	20	49	10	20	99	11.2	31.0	44.9	-80	-220	9.8	10.6	15.8	Example

CLAIMS

[Claim 1]

A CO_2-immobilizing expansive material comprising an ettringite-generating compound that generates ettringite.

[Claim 2]

The CO_2-immobilizing expansive material according to claim 1, wherein the ettringite-generating compound contains free lime as a mineral composition.

[Claim 3]

The CO_2-immobilizing expansive material according to claim 2, comprising 10 to 70 mass% of the free lime.

[Claim 4]

The CO_2-immobilizing expansive material according to claim 1, wherein the ettringite-generating compound contains hauyne as a mineral composition.

[Claim 5]

The CO_2-immobilizing expansive material according to claim 1, wherein the ettringite-generating compound contains ternesite and/or gehlenite as a mineral composition.

[Claim 6]

The CO_2-immobilizing expansive material according to claim 5, wherein a content of the ternesite and the gehlenite in the ettringite-generating compound is 2 to 15 mass%.

[Claim 7]

The CO_2-immobilizing expansive material according to claim 1, wherein a Blaine specific surface area is 2000 to 6000 cm^2/g.

[Claim 8]

The CO_2-immobilizing expansive material according to claim 1, for use mixed with cement.

[Claim 9]

A cement composition comprising the CO_2-immobilizing expansive material according to any one of claims 1 to 8 and cement.

[Claim 10]

A concrete composition comprising the CO_2-immobilizing expansive material according to any one of claims 1 to 8, cement, and an aggregate.