DESCRIPTION

TITLE OF INVENTION: AGENT FOR ACCELERATING PRODUCTION OF CALCIUM CARBONATE HAVING VATERITE-TYPE CRYSTAL STRUCTURE

TECHNICAL FIELD

[0001]

The present invention relates to agents for promoting production of calcium carbonate having a vaterite crystal structure. More specifically, the present invention relates to an agent for promoting production of calcium carbonate having a vaterite crystal structure, the agent being useful for production of calcium carbonate concrete and the like.

BACKGROUND ART

[0002]

The amount of CO_2 emitted by the cement industry accounts for about 8% of the CO_2 emitted by all industries, and reducing the amount of CO_2 emitted in the field of the cement industry is an important issue.

As a measure for reducing CO_2 emissions, a technology has been developed in which emitted CO_2 is recovered and the recovered CO_2 is injected into cement to produce concrete. CO_2 reacts with a calcium component in cement and is fixed as calcium carbonate. Since the concrete thus obtained is excellent in strength, the amount of cement used can be reduced compared with that used to produce ordinary concrete.

As another measure for reducing CO_2 emissions, a technology for producing concrete by using waste, such as waste concrete or concrete sludge, as a raw material and reacting CO_2 with calcium in the raw material has also attracted attention in recent years.

[0003]

Calcium carbonate exists with any one of three crystal structures: calcite, aragonite, and vaterite.

When a calcium slurry such as a calcium hydroxide slurry or a cement slurry is reacted with carbon dioxide, calcite is usually formed as thermodynamically stable calcium carbonate. Meanwhile, Non-Patent Literature 1 proposes that vaterite is synthesized by adding an organic compound having an amino group or a carboxyl group

to calcium hydroxide and subjecting the resulting mixture to carbonation treatment in an aqueous system.

Further, Patent Literature 1 discloses a method for producing vaterite in which, under predetermined conditions, a particulate mixture containing calcium in the form of oxide and/or hydroxide is treated with a reaction medium containing an acid salt of an organic amine.

[0004]

It is known that when thermodynamically unstable vaterite is heated in the presence of a magnesium salt, the vaterite transforms into aragonite. Regarding aragonite, Non-Patent Literature 2 proposes that formation of aragonite in concrete increases the strength of the concrete.

CITATION LIST

- Patent Literature

[0005]

Patent Literature 1: JP H05-509282 T

- Non-Patent Literature

[0006]

Non-Patent Literature 1: I. Matsushita and four others, “Journal of the Ceramic Society of Japan,” Japan, 1996, Vol. 104, pp. 1081-1084

Non-Patent Literature 2: N. K. Bui and seven others, “Journal of Advanced Concrete Technology,” Japan, 2022, Vol. 20, pp. 691-702

SUMMARY OF INVENTION

- Technical Problem

[0007]

Conventionally, in order to reduce CO_2 emissions, wider use has been demanded for technologies for fixing carbon dioxide in cement and for concrete produced using recycled waste concrete and the like. Also, concrete usable as a building material is required to have excellent strength.

[0008]

The present invention has been made in view of the above circumstances, and aims to provide concrete having sufficient strength while reducing CO_2 emissions.

- Solution to Problem

[0009]

The present inventors conducted various studies on a method for increasing the strength of concrete obtained from waste concrete and the like and carbon dioxide as raw materials, and focused on the fact that the crystal structure of calcium carbonate contained in concrete having absorbed carbon dioxide affects the strength of the concrete.

The present inventors found that calcium carbonate having a vaterite crystal structure can be produced in a high proportion by using a compound having a plurality of amino groups in reacting a raw material containing a predetermined amount or more of calcium silicate hydrate, such as waste concrete, with carbon dioxide. They also found that the vaterite calcium carbonate is transformed into an aragonite form when heated, whereby high-strength concrete can be obtained.

As described above, although methods for synthesizing vaterite using calcium hydroxide or calcium oxide as a raw material are known, production of vaterite calcium carbonate using waste concrete or the like as a raw material has not been proposed to date.

The present inventors conceived that the above problem can be successfully solved, and arrived at the present invention.

[0010]

The present invention encompasses the following agent for promoting production of calcium carbonate having a vaterite crystal structure, and the like.

<1> An agent for promoting production of calcium carbonate having a vaterite crystal structure,

the agent containing a compound having a plurality of amino groups, the agent being for use in reacting a composition containing 5% by mass or more of calcium silicate hydrate with carbon dioxide.

<2> The agent for promoting production of calcium carbonate having a vaterite crystal structure according to <1> above,

wherein the composition contains at least one selected from the group consisting of concrete sludge, a hardened hydraulic cement material, and a calcium silicate board.

<3> The agent for promoting production of calcium carbonate having a vaterite crystal structure according to <1> or <2> above,

wherein the compound having a plurality of amino groups is ethylenediamine

and/or polyethyleneimine.

<4> A composition containing:

vaterite calcium carbonate;

a compound having a plurality of amino groups; and

a silicon-containing compound,

a proportion of the vaterite calcium carbonate being 3% by mass or more based on 100% by mass of the composition.

<5> A method for producing calcium carbonate having a vaterite crystal structure,

the method including a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups,

a proportion of the calcium silicate hydrate in the composition being 5% by mass or more based on 100% by mass of the composition.

<6> The method for producing calcium carbonate having a vaterite crystal structure according to <5> above,

wherein the carbonation step is performed by a wet process.

<7> A method for promoting transformation of calcium carbonate into an aragonite crystal structure,

the method including:

a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups; and

a step of heating the composition obtained in the carbonation step,

a proportion of the calcium silicate hydrate in the composition used in the carbonation step being 5% by mass or more based on 100% by mass of the composition.

<8>] The method for promoting transformation of calcium carbonate into an aragonite form according to <7> above,

wherein the carbonation step is performed by a wet process.

<9> A method for producing calcium carbonate concrete,

the method including:

a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups: and

a step of heating the composition obtained in the carbonation step,

a proportion of the calcium silicate hydrate in the composition used in the

carbonation step being 5% by mass or more based on 100% by mass of the composition.

<10> The method for producing calcium carbonate concrete according to <9> above, wherein the carbonation step is performed by a wet process.

<11> The method for producing calcium carbonate concrete according to <9> or <10>, wherein concrete obtained by the method for producing calcium carbonate concrete has a compressive strength of 1 MPa or more.

- Advantageous Effects of Invention

[0011]

The agent for promoting production of calcium carbonate having a vaterite crystal structure of the present invention has the above configuration. Production of calcium carbonate having a vaterite crystal structure can be promoted by using the agent in reacting a composition containing 5% by mass or more of calcium silicate hydrate with carbon dioxide. Use of the vaterite calcium carbonate thus obtained as a raw material for concrete can form aragonite in the concrete and increase the strength of the concrete. Therefore, the agent of the present invention can be suitably used for production of concrete and the like.

DESCRIPTION OF EMBODIMENTS

[0012]

Preferred embodiments of the present invention are specifically described below; however, the present invention is not limited only to the following description, and may be appropriately modified and applied without departing from the gist of the present invention. Combinations of two or more of the preferred embodiments of the present invention described herein are also considered to be preferred embodiments of the present invention.

[0013]

[Agent for Promoting Production of Vaterite-Type Calcium Carbonate]

The agent for promoting production of calcium carbonate having a vaterite crystal structure of the present invention (hereinafter also referred to as a vaterite calcium carbonate production promoting agent or simply a promoting agent) contains a compound having a plurality of amino groups and is used in reacting a composition containing 5% by mass or more of calcium silicate hydrate with carbon dioxide.

Calcium carbonate having a vaterite crystal structure can be produced in a high proportion by using the promoting agent in reacting a composition containing 5% by

mass or more of calcium silicate hydrate (hereinafter also referred to as CSH) with carbon dioxide.

CSH is a main component responsible for the hardening of concrete and also has low solubility in water. It was unexpected for those skilled in the art that vaterite calcium carbonate could be produced in a high proportion using calcium silicate hydrate as a raw material. In this respect, the present invention has significant technical advantages.

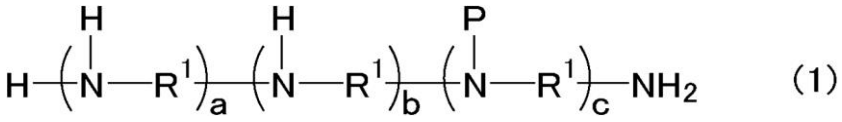
[0014]

The compound having a plurality of amino groups (hereinafter also referred to as a polyamine compound) may be a compound having two or more groups each containing a nitrogen atom, selected from the group consisting of a primary amino group, a secondary amino group, a tertiary amino group, a quaternary ammonium group, and an imino group.

The polyamine compound is preferably represented by the following formula (1):

[0015]

[Chem. 1]



(1)

[0016]

wherein R^1's are the same as or different from each other and each represent a C2-C6 linear alkylene group or a C3-C6 branched alkylene group; P's are the same as or different from each other and each represent a hydrogen atom or a structural unit having another amino group as a branch; and a, b, and c are the same as or different from each other and each represent an integer of 0 or 1 or more, the total of a, b, and c being 1 or more.

[0017]

When P in the formula (1) is a structural unit having another amino group, the structural unit having another amino group is preferably represented by the following formula (2) and is preferably bonded to the structure represented by the formula (1) via an $R^{1'}$ group.

Examples of the C2-C6 linear alkylene group include an ethylene group, an n-propylene group, an n-butylene group, an n-pentylene group, and an n-hexylene group.

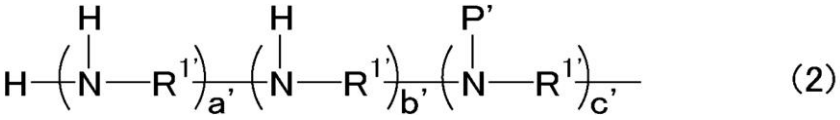
Examples of the C3-C6 branched alkylene group include an isopropylene

group, an isobutylene group, a sec-butylene group, a tert-butylene group, an isopentylene group, and a neopentylene group.

R^1 is preferably an ethylene group, an n-propylene group, an n-butylene group, an isopropylene group, an isobutylene group, or the like, more preferably an ethylene group or an n-butylene group, still more preferably an ethylene group.

[0018]

[Chem. 2]



(2)

[0019]

In the formula (2), a', b', c', P', and R^1' are respectively the same as a, b, c, P, and R^1 in the formula (1).

[0020]

The number of amino groups in the polyamine compound is not limited as long as it is 2 or more, and is preferably 2 to 60. The number is more preferably 2 to 30, still more preferably 2 to 20, particularly preferably 2 to 15.

[0021]

Specific examples of the polyamine compound include polyalkylene polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, tetrabutylenepentamine, pentaethylenehexamine, and hexaethyleneheptamine; polyalkyleneimines such as polyethyleneimine; polyamidoamines; polyvinylamines; polyallylamines; N-alkyl polyalkylene polyamines such as N,N,N',N'-tetramethylethylenediamine and N,N,N',N",N"-pentamethyldiethylenetriamine; and heterocyclic polyamines such as 2-methylpiperazine.

The polyamine compound is more preferably a polyalkylene polyamine or a polyalkyleneimine, still more preferably a polyethylenepolyamine or polyethyleneimine, particularly preferably ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, or polyethyleneimine.

[0022]

The molecular weight of the polyalkylene polyamine compound is not limited, and is preferably 50 to 1000. The molecular weight is more preferably 50 to 500, still more preferably 50 to 300.

When the polyamine compound is a polyalkyleneimine, the weight-average molecular weight of the polyalkyleneimine is preferably 600 or more. The weight-average molecular weight of the polyalkyleneimine is preferably 1,000,000 or less, more preferably 600 to 100,000, still more preferably 600 to 10,000. The molecular weight range described above for the polyalkyleneimine preferably also applies to polyamidoamines, polyvinylamines, and polyallylamines.

The weight-average molecular weight of the polyalkyleneimine can be measured by a GPC analysis method.

[0023]

The proportion of the polyamine compound in the promoting agent is not limited, and is preferably 0.01 to 100% by mass based on 100% by mass of the promoting agent. The proportion is more preferably 10 to 100% by mass, still more preferably 50 to 100% by mass, particularly preferably 70 to 100% by mass, most preferably 100% by mass.

[0024]

The promoting agent may contain a component different from the polyamine compound. Non-limiting examples of the different component include polyethylene glycol derivatives.

The proportion of the different component is not limited, and is preferably 0 to 99% by mass based on 100% by mass of the promoting agent. The proportion is more preferably 0 to 50% by mass, still more preferably 0 to 30% by mass, particularly preferably 0 to 10% by mass, most preferably 0% by mass.

[0025]

The promoting agent is used for a composition containing 5% by mass or more of calcium silicate hydrate.

The composition may be any composition containing 5% by mass or more of CSH. The proportion of CSH is preferably 5 to 100% by mass, more preferably 10 to 80% by mass, still more preferably 20 to 70% by mass, based on 100% by mass of the composition.

Specific examples of the composition containing 5% by mass or more of CSH include concrete sludge, fresh concrete, a hardened hydraulic cement material, and a calcium silicate board.

In a preferred embodiment of the present invention, the composition contains at least one selected from the group consisting of concrete sludge, fresh concrete, a hardened hydraulic cement material, and a calcium silicate board.

Examples of the fresh concrete include fresh concrete to be discarded, such as residual concrete, residual mortar, returned concrete, and returned mortar. Examples of the hardened hydraulic cement material include waste concrete and waste mortar, such as concrete rubble, concrete waste, and waste ALC panels. Of these, concrete sludge, residual concrete, returned concrete, and waste concrete are preferred.

[0026]

[Vaterite-Type Calcium Carbonate-Containing Composition]

The present invention also relates to a composition containing vaterite calcium carbonate, a compound having a plurality of amino groups, and a silicon-containing compound, a proportion of the vaterite calcium carbonate being 3% by mass or more based on 100% by mass of the composition.

Since the vaterite calcium carbonate transforms into an aragonite form when heated, a composition containing a large amount of aragonite-type calcium carbonate can be produced by heat-treating a composition containing a large amount of vaterite calcium carbonate.

Since aragonite-type calcium carbonate contributes to an increase in the strength of concrete, it is useful not only as a conventional recycled aggregate but also as a concrete paste.

Further, vaterite calcium carbonate is useful as a raw material for concrete also because it can be easily fluidized with a cement additive such as a polycarboxylic acid-based dispersant.

[0027]

The proportion of the vaterite calcium carbonate in the composition may be 3% by mass or more, preferably 5% by mass or more, more preferably 30% by mass or more, still more preferably 50% by mass or more, based on 100% by mass of the composition.

The proportion of the vaterite calcium carbonate can be calculated based on the peak intensity in XRD.

[0028]

The vaterite calcium carbonate in the composition preferably has a BET specific surface area of 0.1 to 500 m^2/g. The BET specific surface area is more preferably 1 to 100 m^2/g, still more preferably 10 to 70 m^2/g.

The BET specific surface area can be measured by the method described in the Examples.

[0029]

Specific examples and preferred embodiments of the compound having a plurality of amino groups (polyamine compound) in the composition are as described above.

The proportion of the polyamine compound in the composition is not limited, and the amount thereof is preferably 0.01 to 100% by mass relative to 100% by mass of the vaterite calcium carbonate. The amount is more preferably 0.01 to 10% by mass, still more preferably 0.01 to 5% by mass, particularly preferably 0.01 to 1% by mass, most preferably 0.01% by mass.

[0030]

The proportion of the polyamine compound in the composition is not limited, and the amount thereof is preferably 0.001 to 40% by mass relative to 100% by mass of the calcium element in the composition. The amount is more preferably 0.01 to 20% by mass, still more preferably 0.05 to 10% by mass, particularly preferably 0.1 to 5% by mass, most preferably 0.3 to 2.5% by mass.

[0031]

The silicon-containing compound in the composition is not limited as long as it contains a silicon element. Examples thereof include tricalcium silicate, dicalcium silicate, silicon dioxide, aluminum silicate, and tetracalcium aluminoferrite.

[0032]

The proportion of the silicon-containing compound in the composition is not limited, and the amount of silicon element is preferably 0.01 to 100 mol% relative to 100 mol% of calcium element. The amount is more preferably 0.01 to 70 mol%, still more preferably 0.01 to 50 mol%, particularly preferably 0.01 to 30 mol%.

[0033]

[Method for Producing Calcium Carbonate Having Vaterite Crystal Structure]

The present invention also relates to a method for producing calcium carbonate having a vaterite crystal structure, the method including a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups, a proportion of the calcium silicate hydrate in the composition being 5% by mass or more based on 100% by mass of the composition.

In the carbonation step, carbon dioxide is supplied to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups. Thereby, calcium carbonate having a vaterite crystal structure can be produced in a high proportion.

[0034]

The preferred proportion of CSH in the composition used in the carbonation step is as described above. Specific examples and preferred embodiments of the composition containing 5% by mass or more of CSH are also as described above.

[0035]

Specific examples and preferred embodiments of the compound having a plurality of amino groups (polyamine compound) used in the carbonation step are as described above.

The amount of the polyamine compound used in the carbonation step is not limited, and is preferably 0.001 to 40% by mass relative to 100% by mass of calcium element in the raw material used in the carbonation step. The amount is more preferably 0.01 to 20% by mass, still more preferably 0.05 to 10% by mass, particularly preferably 0.1 to 5% by mass, most preferably 0.3 to 2.5% by mass.

[0036]

The amount of carbon dioxide fixed in the carbonation step is not limited, and is preferably 1 to 110% by mass relative to 100% by mass of calcium element in the raw material used in the carbonation step. The amount is more preferably 10 to 110% by mass, still more preferably 30 to 110% by mass, particularly preferably 50 to 110% by mass.

[0037]

The carbonation step is preferably performed by a wet process. Preferably, a slurry composition containing CSH is brought into contact with carbon dioxide gas in the presence of the polyamine compound.

The flow rate of the carbon dioxide gas is not limited, and is preferably 5 cc/min or more per gram of solids in the composition. This further increases the amount of carbon dioxide fixed and improves the carbon dioxide fixation rate. The flow rate of the carbon dioxide gas is more preferably 10 cc/min or more, still more preferably 20 cc/min or more, per gram of solids in the composition. The flow rate of the carbon dioxide gas is preferably 100 cc/min or less per gram of solids of the composition.

[0038]

The duration of carbon dioxide supply in the carbonation step is not limited, and is preferably 0.01 to 24 hours. The duration is more preferably 0.01 to 7 hours, still more preferably 0.5 to 4 hours.

[0039]

The carbon dioxide supply in the carbonation step is preferably performed until the pH of the composition becomes 10 or less. This can further increase the amount of carbon dioxide fixed. The carbon dioxide supply is more preferably performed until the pH becomes 9 or less, still more preferably until the pH becomes 8 or less.

[0040]

The production method is not limited as long as it includes the carbonation step. When the material containing CSH is in lump form or the like, the production method may include a step of pulverizing the lump before the carbonation step.

The pulverization may be performed by any method, and may be performed using a pulverizer commonly used in cement plants and the like, such as a hammer crusher, a roll crusher, a jaw crusher, a vertical mill, a ball mill, a rod mill, or a disk mill.

[0041]

[Method for Producing Calcium Carbonate Concrete]

The present invention also relates to a method for producing calcium carbonate concrete, the method including: a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups: and a step of heating the composition obtained in the carbonation step, a proportion of the calcium silicate hydrate in the composition used in the carbonation step being 5% by mass or more based on 100% by mass of the composition.

Calcium carbonate concrete means concrete obtained using carbon dioxide and a calcium-containing material such as waste concrete as raw materials.

According to the production method of the present invention, concrete can be produced using only waste such as waste concrete, atmospheric carbon dioxide, and water as materials. Such a production method helps address the problems of resource depletion and waste generation.

The carbonation step in the method for producing calcium carbonate concrete is the same as the carbonation step in the above-described method for producing calcium carbonate having a vaterite crystal structure.

[0042]

The heating step in the method for producing calcium carbonate concrete is not limited as long as the composition obtained in the carbonation step is heated. The promotion method preferably includes a step of adding a magnesium salt or a strontium salt to the composition before heating the composition obtained in the carbonation step.

The magnesium salt is not limited as long as it contains magnesium element, and examples thereof include halides, hydroxides, oxides, carbonates, nitrates, sulfates, silicates, phosphonates, and carboxylates. The magnesium salt is preferably a halide, more preferably a chloride.

[0043]

The concentration of the magnesium salt in the composition used in the heating step is not limited, and is preferably 0 to 1 mol/L. The concentration is more preferably 0.01 to 0.5 mol/L, still more preferably 0.01 to 0.2 mol/L.

[0044]

The method for producing calcium carbonate concrete preferably includes a step of adding a base to the composition before heating the composition obtained in the carbonation step.

Non-limiting examples of the base include hydroxides and oxides of alkali metals such as lithium, sodium, and potassium, and alkaline earth metals such as calcium and magnesium. Of these, an alkali metal hydroxide is preferred, and sodium hydroxide is more preferred.

[0045]

The concentration of the base in the composition used in the heating step is not limited, and is preferably 0 to 1 N. The concentration is more preferably 0.001 to 0.5 N, still more preferably 0.01 to 0.3 N.

[0046]

The ratio of liquid to solid (liquid/solid) in the composition used in the heating step is not limited, and is preferably 0.3 to 100. The ratio is more preferably 0.5 to 50, still more preferably 0.5 to 30, particularly preferably 0.5 to 25. In one embodiment, the ratio may be 0.5 to 10, or may be 0.5 to 3.

[0047]

The method for producing calcium carbonate concrete preferably includes a step of adding a solvent such as water to the composition before heating the composition obtained in the carbonation step. The amount of the solvent is not limited. The solvent is preferably added so that the ratio of liquid to solid in the composition falls within the preferred range described above.

[0048]

The method for producing calcium carbonate concrete may include, before heating the composition obtained in the carbonation step, a step of adding aggregates such as fine aggregate or coarse aggregate, a dispersant for cement, and other additives

to the composition.

[0049]

Non-limiting examples of the aggregates include gravel, crushed stone, granulated slag, recycled aggregate, and the like, as well as refractory aggregates such as silica-based, clay-based, zircon-based, high-alumina-based, silicon carbide-based, graphite-based, chrome-based, chrome-magnesia-based, and magnesia-based aggregates. An example of the fine aggregate is sand, and an example of the coarse aggregate is crushed stone.

[0050]

Non-limiting examples of the dispersant for cement (water-reducing agent) include: (i) various sulfonic acid-based dispersants (water-reducing agents) having a sulfonic acid group in the molecule, such as polyalkylarylsulfonate-based dispersants such as naphthalenesulfonic acid-formaldehyde condensates; melamine-formaldehyde resins and sulfonate-based dispersants such as melaminesulfonic acid-formaldehyde condensates; aromatic aminosulfonate-based dispersants such as aminoarylsulfonic acid-phenol-formaldehyde condensates; ligninsulfonate-based dispersants such as ligninsulfonates and modified ligninsulfonates; and polystyrenesulfonate-based dispersants; (ii) various polycarboxylic acid-based dispersants (water-reducing agents) having a (poly)oxyalkylene group and a carboxyl group in the molecule, such as copolymers obtained from a polyalkylene glycol mono(meth)acrylate-based monomer, a (meth)acrylic acid-based monomer, and a monomer copolymerizable with these monomers as described in JP S59-18338 B and JP H07-223852 A, and copolymers obtained from an unsaturated (poly)alkylene glycol ether-based monomer, a maleic acid-based monomer, or a (meth)acrylic acid-based monomer as described in JP H10-236858 A, JP 2001-220417 A, JP 2002-121055 A, and JP 2002-121056 A; and (iii) various phosphoric acid-based dispersants (water-reducing agents), such as copolymers having a (poly)oxyalkylene group and a phosphate ester group in the molecule, including copolymers obtained from an (alkoxy)polyalkylene glycol mono(meth)acrylate, a phosphoric acid monoester-based monomer, and a phosphoric acid diester-based monomer, as described in JP 2006-52381 A; polycondensation products formed from a monomer having a (poly)oxyalkylene group and an aromatic ring group and/or a heterocyclic aromatic group, a monomer having a phosphoric acid (salt) group and/or a phosphate ester group and an aromatic ring group and/or a heterocyclic aromatic group, and an aldehyde compound, as described in JP 2008-517080 T; and dispersants having an aromatic triazine structural unit, a polyalkylene

glycol structural unit, and a phosphate ester structural unit, as described in JP 2015-508384 T.

[0051]

The amount of the dispersant for cement (water-reducing agent) added is not limited, and is preferably 0.01 to 10% by mass relative to 100% by mass of the vaterite-containing powder. The amount is more preferably 0.01 to 1.0% by mass, still more preferably 0.05 to 0.5% by mass, particularly preferably 0.05 to 0.3% by mass.

[0052]

Examples of other additives and the like include cement additives (materials), cement wetting agents, thickeners, segregation-reducing agents, flocculants, drying shrinkage-reducing agents, strength-enhancing agents, self-leveling agents, rust inhibitors, colorants, and antifungal agents, which are exemplified in (1) to (12) below. One or two or more of these may be used.

[0053]

(1) Water-soluble polymer substances: nonionic cellulose ethers such as methyl cellulose, ethyl cellulose, and carboxymethyl cellulose; polysaccharides produced by microbial fermentation, such as yeast glucan, xanthan gum, and β-1,3-glucans; polyacrylamide; and the like.

(2) Polymer emulsions: copolymers of various vinyl monomers, such as alkyl (meth)acrylates; and the like.

(3) Set retarders: oxycarboxylic acids such as gluconic acid, glucoheptonic acid, arabonic acid, malic acid, and citric acid, or salts thereof; sugars and sugar alcohols; polyhydric alcohols such as glycerol; phosphonic acids such as aminotri(methylenephosphonic acid) and derivatives thereof; and the like.

(4) Early-strength agents and accelerators: soluble calcium salts such as calcium chloride, calcium nitrite, calcium nitrate, calcium bromide, and calcium iodide; chlorides such as iron chloride and magnesium chloride; sulfates; potassium hydroxide; sodium hydroxide; carbonates; thiosulfates; formic acid and formates such as calcium formate; alkanolamines; alumina cement; calcium aluminate silicate; and the like.

(5) Oxyalkylene-based defoaming agents: polyoxyalkylene alkyl ethers such as diethylene glycol heptyl ether; polyoxyalkylene acetylene ethers; (poly)oxyalkylene fatty acid esters; polyoxyalkylene sorbitan fatty acid esters; polyoxyalkylene alkyl(aryl) ether sulfate salts; polyoxyalkylene alkyl phosphate esters; polyoxyalkylene alkylamines such as polyoxypropylene polyoxyethylene laurylamine (e.g., an adduct with 1 to 20 mol of propylene oxide and 1 to 20 mol of ethylene oxide) and fatty acid-

derived amines obtained from hardened tallow to which an alkylene oxide has been added (e.g., an adduct with 1 to 20 mol of propylene oxide and 1 to 20 mol of ethylene oxide); polyoxyalkylene amides; and the like.

(6) Defoaming agents other than oxyalkylene-based defoaming agents: mineral oil-based, fat and oil-based, fatty acid-based, fatty acid ester-based, alcohol-based, amide-based, phosphate ester-based, metal soap-based, and silicone-based defoaming agents, and the like.

[0054]

(7) AE agents: resin soaps, saturated or unsaturated fatty acids, sodium hydroxystearate, lauryl sulfate, ABS (alkylbenzene sulfonic acid), alkanesulfonates, polyoxyethylene alkyl(phenyl) ethers, polyoxyethylene alkyl(phenyl) ether sulfate esters or salts thereof, polyoxyethylene alkyl(phenyl) ether phosphate esters or salts thereof, protein materials, alkenyl sulfosuccinic acid, α-olefin sulfonates, and the like.

(8) Other surfactants: various anionic surfactants; various cationic surfactants such as alkyltrimethylammonium chloride; various nonionic surfactants; various amphoteric surfactants; and the like.

(9) Waterproofing agents: fatty acids (salts), fatty acid esters, fats and oils, silicones, paraffin, asphalt, waxes, and the like.

(10) Rust inhibitors: nitrites, phosphates, zinc oxide, and the like.

(11) Crack-reducing agents: polyoxyalkyl ethers and the like.

(12) Expansive materials: ettringite-based materials, coal-based materials, and the like.

[0055]

The heating temperature of the composition in the heating step is not limited, and is preferably 30°C to 100°C. The heating temperature is more preferably 40°C to 95°C, still more preferably 60°C to 95°C.

[0056]

The heating duration in the heating step is not limited, and is preferably 1 to 200 hours. The heating duration is more preferably 5 to 200 hours, still more preferably 5 to 72 hours. In one embodiment, the heating duration may be 1 to 20 hours, or may be 1 to 10 hours.

[0057]

According to the method for producing calcium carbonate concrete of the present invention, concrete having high compressive strength can be produced.

The compressive strength of concrete obtained by the production method is

preferably 1 MPa or more. The compressive strength is more preferably 5 MPa or more, still more preferably 10 MPa or more.

The compressive strength of the concrete can be measured by the method described in the Examples.

[0058]

[Method for Promoting Transformation of Calcium Carbonate into Aragonite Form]

The present invention also relates to a method for promoting transformation of calcium carbonate into an aragonite crystal structure, the method including: a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups; and a step of heating the composition obtained in the carbonation step, a proportion of the calcium silicate hydrate in the composition used in the carbonation step being 5% by mass or more based on 100% by mass of the composition.

[0059]

The carbonation step in the method for promoting transformation of calcium carbonate into an aragonite form is the same as the carbonation step in the method for producing calcium carbonate having a vaterite crystal structure described above.

The heating step in the method for promoting transformation of calcium carbonate into an aragonite form is the same as the heating step in the method for producing calcium carbonate concrete described above.

[0060]

[Use of Compound Having Plurality of Amino Groups for Promoting Transformation of Calcium Carbonate into Aragonite Form]

The present invention also relates to use of a compound having a plurality of amino groups for promoting transformation of calcium carbonate into an aragonite form, the use including a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups. The proportion of the calcium silicate hydrate in the composition is 5% by mass or more based on 100% by mass of the composition.

The carbonation step in the above-described use is the same as the carbonation step in the method for producing calcium carbonate having a vaterite crystal structure described above.

EXAMPLES

[0061]

The present invention is described in more detail below with reference to examples, but the present invention is not limited only to these examples. Unless otherwise specified, “part(s)” means “part(s) by weight” and “%” means “% by mass”.

[0062]

The molecular weight of the polyamines was measured as follows.

(Molecular Weight Measurement (GPC Analysis Method))

The weight-average molecular weight and number-average molecular weight in the present invention can be measured by a known gel permeation chromatography (GPC) method using pullulan as a standard. In the present invention, the GPC measurement was performed under the following conditions.

Measurement device: available from Shimadzu Corporation

Columns used: SHODEX OHpak SB-807HQ (two columns) + SB-806M/HQ (two columns), available from Showa Denko K.K.

Eluent: adjusted to 0.5 mol% sodium nitrate and 0.5 mol% acetic acid

Standard: pullulan P-82 (available from FUJIFILM Wako Pure Chemical Corporation)

Detector: differential refractometer (available from Shimadzu Corporation)

Flow rate: 0.4 mL/min

[0063]

(Experimental Instruments and Procedures)

A composition was prepared by adding an additive and water to concrete sludge or a pulverized material of simulated waste concrete in a container, carbon dioxide gas was passed through the composition for a predetermined time at room temperature, the composition was filtered to collect a powder, and the powder was dried. The resulting powder was subjected to measurement of weight loss rate using a TG-DTA instrument (instrument name: STA200, available from Hitachi High-Tech Science Corporation), the amount of calcium carbonate generated was calculated, and the degree of carbonation was calculated. The crystal polymorph of calcium carbonate contained in the powder was analyzed by XRD (instrument name: D2 PHASER, available from Bruker Corporation). Details are shown below.

Cement: cement (ordinary Portland cement (OPC), available from Taiheiyo Cement Corporation)

Preparation of pulverized material of simulated waste concrete:

A cement paste having w/c of 0.4 was prepared (kneading was performed by a method in accordance with JIS R 5201). The kneaded paste was packed into a mold

(Φ50 × 50 × 100 mm), air-cured at 20°C for 3 days, demolded 3 days after water addition, and cured in water for 11 days. After curing, the hardened body was pulverized and sieved with a 100-μm sieve to obtain a powder having a particle size of 100 μm or less. The powder was collected and used for the test.

CO_2 blowing method (in the case of simulated waste concrete):

The powder was added to ion-exchanged water at a ratio of w/b = 5 to 50 (W: additive and water; B: pulverized material of waste concrete), followed by stirring at a constant speed using a stirring rod. When an additive was used, the additive was added to the ion-exchanged water before use. Carbon dioxide gas (available from Sumitomo Seika Chemicals Co., Ltd.) was flowed through the slurry at room temperature at a flow rate of 0.3 L/min for a predetermined time. Then, the filtrate was filtered. The resulting powder was washed with acetone, dried at 40°C (under a nitrogen atmosphere) for 24 hours, and subjected to TG-DTA analysis and XRD analysis.

CO_2 blowing method (in the case of concrete sludge)

The powder was added to ion-exchanged water at a ratio of w/b = 0.4 (W: additive and water; B: ordinary Portland cement), followed by stirring at a constant speed for four hours using a stirring rod. After four hours, ion-exchanged water was additionally introduced so that the ratio of w/b reached a predetermined ratio. When an additive was used, the additive was added to the ion-exchanged water to be additionally introduced before use. Carbon dioxide gas (available from Sumitomo Seika Chemicals Co., Ltd.) was flowed through the slurry at room temperature at a flow rate of 0.3 L/min for a predetermined time. Then, the filtrate was filtered. The resulting powder was washed with acetone, dried at 40°C (under a nitrogen atmosphere) for 24 hours, and subjected to TG-DTA analysis and XRD analysis.

[0064]

(Measurement of Amount of Calcium Carbonate)

The amount of calcium carbonate was quantified by the following measurement method using TG-DTA.

Conditions: measurement was performed under a nitrogen atmosphere at a temperature rise rate of 20°C/min.

Analysis: the mass loss around 600°C to 800°C as measured by TG-DTA was regarded as the mass loss due to decarbonation of calcium carbonate, and the amount of calcium carbonate was calculated. The degree of carbonation was determined as follows, with the degree of carbonation when all calcium oxide in the cement or waste

concrete reacted with carbon dioxide being taken as 100%.

In order to quantify the amount of calcium oxide in the powder, the chemical composition of the cement or pulverized material of waste concrete was analyzed in accordance with JIS R 5202:2015 and JIS R 5204:2019 (X-ray fluorescence analysis method for cement) using an X-ray fluorescence spectrometer (device name: ZSX PrimusII, available from Rigaku Corporation). Specifically, the mass ratio of calcium element was determined, and the mass ratio of calcium oxide was calculated based thereon. The results are shown in Table 1.

[Table 1]

	Ca (mass%)	CaO (mass%)
OPC (Taiheiyo Cement)	41.00	57.37
Simulated waste concrete	41.20	57.65

[0065]

(Measurement of Calcium Carbonate Crystal Polymorph)

The crystal polymorph of calcium carbonate was measured by the following measurement method using XRD.

Conditions: measurement was performed using a Cu Kα target at a tube voltage of 45 kV, a tube current of 40 mA, a scan range of 5 to 70 deg 2θ, and a step width of 0.02 deg.

Analysis: the ratio of each crystal polymorph was calculated using the following equations, where Ic is the peak intensity of the (104) plane for calcite, Ia is the peak intensity of the (221) plane for aragonite, and Iv is the peak intensity of the (110) plane for vaterite.

Here, Xc is the weight fraction of calcite, Xa is the weight fraction of aragonite, and Xv is the weight fraction of vaterite, and Xc + Xa + Xv = 1 is assumed to be satisfied.

$Xa = 3.175 \times Ia/(Ic + 3.175 \times Ia + 7.691 \times Iv)$

$Xc = Ic \times Xa/(3.157 \times Ia)$

(Transformation to Aragonite)

The vaterite-containing powder obtained by the CO_2 blowing was added to a solution having a predetermined solvent composition and heated for a predetermined time. The heated slurry was filtered under reduced pressure, and the obtained powder was washed with acetone, dried at room temperature (under a nitrogen atmosphere) for 24 hours, and subjected to XRD analysis.

[0066]

<Production Example 1> Production of Water-Reducing Agent (Polycarboxylic Acid Copolymer α)

A glass reaction vessel equipped with a thermometer, a stirrer, a dropping funnel, and a reflux condenser was charged with 72.26 parts of ion-exchanged water and 127.74 parts of an unsaturated alcohol obtained by adding 50 mol of ethylene oxide to 3-methyl-3-buten-1-ol, and the temperature was raised to 65°C. Then, 0.71 parts of a 30% aqueous hydrogen peroxide solution was added thereto, and 46.58 parts of a 40% aqueous acrylic acid solution was added dropwise over three hours, 0.67 parts of 3-mercaptopropionic acid was added dropwise over three hours, and 12.97 parts of a 2.1% aqueous L-ascorbic acid solution was added dropwise over 3.5 hours. Thereafter, the temperature was continuously maintained at 65°C for 60 minutes to complete the polymerization reaction, the temperature was lowered to 50°C or less, and the reaction mixture was neutralized with 76.07 parts of a 12.2% aqueous sodium hydroxide solution so that the pH changed from 4 to 7, thereby obtaining a polycarboxylic acid copolymer in the present invention composed of an aqueous polymer solution having a weight-average molecular weight of 29,000. The amount of all monomers used relative to the total amount of raw materials used during polymerization was 56.2% by weight.

[0067]

<Paste Test>

Preparation of paste sample

The paste test was performed in an environment having a temperature of 20°C ± 1°C and a relative humidity of 60% ± 15%. The mortar formulation was adjusted to satisfy B/W = 140/140 (g).

B: Example 1 (vaterite-containing powder), Comparative Example 1 (calcite-containing powder)

W: the water-reducing agent of Production Example 1 and a defoaming agent in a 0.1 N NaOH or 0.1 N $MgCl_2$ aqueous solution

Using a mortar mixer (mixer available from Hobart Corporation, model number: N-50), B and W were kneaded at speed 1 for four minutes.

[0068]

<Measurement of Compressive Strength>

After kneading, a sample for a compressive strength test was prepared, and the compressive strength after steam curing was measured under the following conditions.

Specimen preparation: 50 mm × 100 mm
Specimen curing: curing was performed for 72 hours at a temperature of 90°C and a humidity of 98% using a constant-temperature and constant-humidity oven.
Compressive strength measurement: automatic compressive strength tester (available from Maekawa Mfg. Co., Ltd.)

[0069]

(Equations for Calculating Degree of Carbonation)

Symbols are indicated in parentheses, and units are indicated in brackets.

Maximum amount of carbon dioxide fixed (A) [g] = amount of calcium oxide (B) [g] in 1 g of powder × m/n

m: molecular weight of carbon dioxide [g/mol]

n: molecular weight of calcium oxide [g/mol]

Maximum weight loss rate (C) = (A)/(1 + (A)) × 100 [%]

Degree of carbonation (D) = weight loss rate/(C) × 100 [%]

*Weight loss rate = mass loss around 600°C to 800°C measured by TG-DTA

The carbonation improvement rate (E) of a sample, where the degree of carbonation without addition (D0) is taken as 100%, is represented by the following equation:

(E) = degree of carbonation of sample (D1)/(D0) × 100 [%].

[0070]

Examples (1) to (11) and Comparative Examples (1) to (5)

As shown in Table 2 below, the degree of carbonation after four hours and the crystal polymorph of calcium carbonate were measured using various additives (agents for promoting production of vaterite calcium carbonate), the experimental apparatus, and procedures described above. The results are shown in Table 2.

[Table 2]

	Additive	Powder	Amount added (wt%/Ca)	L/S	Degree of carbonation	Xv
Example (1)	Ethylenediamine	Simulated waste concrete	2.1	5	89%	93%
Example (2)	Ethylenediamine	Simulated waste concrete	2.1	50	90%	84%
Example (3)	Ethylenediamine	Simulated waste concrete	8.2	50	90%	90%
Example (4)	Ethylenediamine	Simulated waste concrete	16.5	50	-	95%
Example (5)	Diethylenetriamine	Simulated waste concrete	2.1	5	-	93%
Example (6)	Triethylenetetramine	Simulated waste concrete	2.1	5	-	91%
Example (7)	Tetraethylenepentamine	Simulated waste concrete	2.1	5	-	91%
Example (8)	Pentaethylenehexamine	Simulated waste concrete	2.1	5	-	92%
Example (9)	Polyethyleneimine (SP-003, available from Nippon Shokubai Co., Ltd.)	Simulated waste concrete	2.1	5	82%	96%
Example (10)	Ethylenediamine	Concrete sludge	2.1	5	55%	78%
Example (11)	Polyethyleneimine (SP-003, available from Nippon Shokubai Co., Ltd.)	Concrete sludge	2.1	50	-	71%
Comparative Example (1)	No additive	Simulated waste concrete	2.1	5	92%	0%
Comparative Example (2)	No additive	Concrete sludge	2.1	5	84%	0%
Comparative Example (3)	Monoethanolamine	Simulated waste concrete	2.1	5	-	0%
Comparative Example (4)	Triethanolamine	Simulated waste concrete	2.1	5	-	0%
Comparative Example (5)	L-Aspartic acid	Simulated waste concrete	2.1	5	-	0%

[0071]

Various conditions were studied in order to transform the vaterite-containing powder obtained in Example (1) shown in Table 2 into aragonite. The results are shown in Table 3. L/S in Table 3 represents the ratio of liquid to solid (liquid/solid) in the composition.

[Table 3]

	NaOH concentration (N)	$MgCl_2$ concentration (mol/L)	L/S	Heating time	Temperature	Xa
Example (12)	0.01	0.1	50	3	80	25%
Example (13)	0.1	0.1	50	3	80	38%
Example (14)	0.1	0.1	1	7	95	63%
Example (15)	0.1	0.1	25	7	95	93%

[0072]

A sample for a compressive strength test was prepared using the vaterite-containing powder obtained in Example (1) or the powder of Comparative Example (1), shown in Table 2, and after steam curing under the above-described conditions, the compressive strength was measured. The results are shown in Table 4.

[0073]

[Table 4]

	Powder	Compressive strength (MPa)
Example (16)	Example (1)	1.0
Comparative Example (6)	Comparative Example (1)	Not hardened

CLAIMS

[Claim 1] An agent for promoting production of calcium carbonate having a vaterite crystal structure,

the agent comprising a compound having a plurality of amino groups, the agent being for use in reacting a composition containing 5% by mass or more of calcium silicate hydrate with carbon dioxide.

[Claim 2] The agent for promoting production of calcium carbonate having a vaterite crystal structure according to claim 1,

wherein the composition contains at least one selected from the group consisting of concrete sludge, a hardened hydraulic cement material, and a calcium silicate board.

[Claim 3] The agent for promoting production of calcium carbonate having a vaterite crystal structure according to claim 1 or 2,

wherein the compound having a plurality of amino groups is ethylenediamine and/or polyethyleneimine.

[Claim 4] A composition comprising:

vaterite calcium carbonate;

a compound having a plurality of amino groups; and

a silicon-containing compound,

a proportion of the vaterite calcium carbonate being 3% by mass or more based on 100% by mass of the composition.

[Claim 5] A method for producing calcium carbonate having a vaterite crystal structure,

the method comprising a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups,

a proportion of the calcium silicate hydrate in the composition being 5% by mass or more based on 100% by mass of the composition.

[Claim 6] The method for producing calcium carbonate having a vaterite

crystal structure according to claim 5,

wherein the carbonation step is performed by a wet process.

[Claim 7] A method for promoting transformation of calcium carbonate into an aragonite crystal structure,

the method comprising:

a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups; and

a step of heating the composition obtained in the carbonation step,

a proportion of the calcium silicate hydrate in the composition used in the carbonation step being 5% by mass or more based on 100% by mass of the composition.

[Claim 8] The method for promoting transformation of calcium carbonate into an aragonite form according to claim 7,

wherein the carbonation step is performed by a wet process.

[Claim 9] A method for producing calcium carbonate concrete,

the method comprising:

a carbonation step including supplying carbon dioxide to a composition containing calcium silicate hydrate in the presence of a compound having a plurality of amino groups: and

a step of heating the composition obtained in the carbonation step,

a proportion of the calcium silicate hydrate in the composition used in the carbonation step being 5% by mass or more based on 100% by mass of the composition.

[Claim 10] The method for producing calcium carbonate concrete according to claim 9,

wherein the carbonation step is performed by a wet process.

[Claim 11] The method for producing calcium carbonate concrete according to claim 9 or 10,

wherein concrete obtained by the method for producing calcium carbonate concrete has a compressive strength of 1 MPa or more.