

CEMENT COMPOSITION, CONSTRUCTION METHOD USING THE SAME, AND METHOD FOR PRODUCING THE SAME

TECHNICAL FIELD

[0001] The present invention relates mainly to a cement composition used in civil engineering and construction industries.

BACKGROUND ART

[0002] Cement-based materials usually used in the civil engineering / construction industries require complicated and burdensome labor procedures, from mixing, molding to curing. Simplification and mitigation of such procedures have been demanded, due to a decrease in the population of labor and craftsmanship. From the viewpoint of such a background, some methods have been taken, for example, facilitating the mixing of concrete and using quick-hardening concrete for enabling such procedures time to be shorten.

[0003] Patent Document 1 discloses an improved method in which an introduction of an automated concrete mixing device can simplify and reduce the procedures, but such a special mixing device might increase the concrete cost. Patent Document 2 discloses a quick-hardening concrete allowing to be accessed early without using special curing. However, there is a problem that a complicated mixing procedure is required as the same as ordinary concrete.

CITATION LIST

Patent Literature

[0004]

Patent Document 1: Japanese Patent Application Laid-open Publication No. 2016-060134A

Patent Document 2: Japanese Patent Application Laid-open Publication No. 2002-356363A

Patent Document 3: Japanese Patent Application Laid-open Publication No. H04-132644A

SUMMARY OF INVENTION

Technical Problem

[0005] Usually, a mixing procedure of the cement-based material and water is essential

to the use of a cement-based material. For this procedure, a dedicated mixing device is required, but it has often been difficult to bring the mixing device into mountainous areas hard to transport. In addition, it is inefficient to perform the mixing procedure each time for a small volume such as a pothole generated on the road surface. Furthermore, generation of dust during the mixing procedure might incur complaints from surrounding houses. A pothole refers to a hole formed in the pavement surface of a road due to repeated load by vehicles passing through the road, road shape, or pavement stagnant water.

[0006] Patent Document 3 discloses a non-mixing method in which a mortar material composed of cement, a cement hardened material, and a fine aggregate having a maximum particle diameter of 2.5 mm and a particle diameter of 0.5 mm or less at a rate of 50 to 80% is put into water and cured. However, such a conventional method could not solve problems that the resulting cured products have insufficient water permeability and poor compressive strength.

Solution to Problem

[0007] As a result of studies of the above-mentioned problems and demands, the present inventors has found that use of a specific aggregate and calcium aluminate in combination enables a cement composition to be cured without requiring mixing, and have completed the present invention.

[0008] The present invention can provide the below embodiments.

[0009] (1) A cement composition which is not required to be mixed, comprising:
cement;
calcium aluminate; and
aggregate,

wherein the calcium aluminate has 1.0 or more and 3.0 or less of a $\text{CaO} / \text{Al}_2\text{O}_3$ molar ratio, and

wherein the aggregate has a particle diameter of 2.5 mm or more at a rate of 30% or more.

[0010] (2) The cement composition which is not required to be mixed according to (1), further comprising a setting modifier with a carboxylic acid structure.

[0011] (3) The cement composition which is not required to be mixed according to (1) or (2), further comprising an alkali metal inorganic salt as a setting modifier.

[0012] (4) The cement composition which is not required to be mixed according to any one of (1) to (3), further comprising polysaccharide gum.

[0013] (5) A construction method, comprising:
filling a target portion with the cement composition which is not required to be mixed according to any one of (1) to (4); and
watering over the filled cement composition.

[0014] (6) A method for producing a cement composition which is not required to be mixed, the method comprising:

mixing, without an addition of gypsum, cement, calcium aluminate with 1.0 or more and 3.0 or less of a $\text{CaO} / \text{Al}_2\text{O}_3$ molar ratio, and an aggregate having a particle diameter of 2.5 mm or more at a rate of 30% or more.

Advantageous Effects of Invention

[0015] Filling a target portion with the cement composition according to the embodiment of the present invention and watering over the filled cement composition as necessary enables the cement composition to be cured in a short time of 10 minutes without requiring mixing the cement materials and water, or special curing procedures such as rolling procedure, heating, and moisturizing after construction.

DESCRIPTION OF EMBODIMENTS

[0016] The present invention will be described as the below in detail. Parts and percentages (%) referred to herein show standard weight (mass), unless otherwise specified. A numerical range referred to herein includes its upper limit value and its lower limit value, unless otherwise specified. A cement composition referred to herein is defined as containing cement, calcium aluminate, and aggregate, and may further contain a setting modifier and a polysaccharide gum.

[0017] The cement contained in the present cement composition may include any portland cements such as normal, high early strength, super high strength, low heat, moderate heat, any Portland cements mixed with blast furnace slag, fly ash, and silica,

and any filler cements mixed with limestone powder, and air-cooled blast furnace slag. Furthermore, it may include eco-cement, which is environmentally friendly cement manufactured by municipal waste incineration ash or sewage sludge incineration ash as a raw material. In the embodiment of the present invention, one or more of the above can be used in combination.

[0018] The calcium aluminate contained in the cement composition may be a compound obtained by mixing a calcia raw material and an alumina raw material and firing such mixed materials in a kiln, or mainly composed of crystalline and amorphous CaO and Al₂O₃ obtained by melting in an electric furnace and cooling. The calcium aluminate used for the present invention may include alumina cement, and alumina cement No. 1, and alumina cement No. 2, which are commercially available, can be used. Furthermore, amorphous calcium aluminate may preferably be used, which can be obtained by melting in an electric furnace and rapidly cooling, and which has a shorter hardening time than alumina cement and providing high initial strength development thereafter. The CaO / Al₂O₃ molar ratio (hereafter referred to as C / A molar ratio) in the calcium aluminate may be 1.0 or more and 3.0 or less, and may preferably be 1.7 or more and 2.5 or less. Even when the calcium aluminate has a small value of the C / A molar ratio, which 1.0 to 1.7, it can be shorten the hardening time and increase the initial strength development, by adding cement, slaked lime, and quicklime. The cement composition according to the present invention may be preferably manufactured without an addition of gypsum, from the viewpoint of increase the strength of the cured product. As the reason of increasing the strength, it is considered that when calcium aluminate alone is used as a quick-hardening material, different hydrates such as C₂AH₈ (= 2CaO • Al₂O₃ • 8H₂O) and C₃AH₆ (= 3CaO • Al₂O₃ • 6H₂O) are formed, on the other hand the conventional combination with the calcium aluminate and gypsum as the quick-hardening material produces ettringite as a hydrate during hydration.

[0019] The components other than CaO and Al₂O₃ contained in the calcium aluminate may preferably be 15% or less, and may more preferably be 10% or less, from the viewpoint of initial strength development. If it exceeds 15%, it takes much time to harden and might not harden in a low temperature environment. As a representative example of the components other than CaO and Al₂O₃, silicon dioxide may be contained; alkali metal oxides, alkaline earth metal oxides, titanium oxide, iron oxide, alkali metal halides, alkaline earth metal halides, alkali metal sulfates, and alkaline earth metal sulfates may be contained, but not limited to them.

[0020] The vitrification rate of the amorphous calcium aluminate may preferably be 70% or more, and may more preferably be 90% or more. If it is less than 70%, the initial strength development might decrease. For the vitrification rate, a powder X-ray diffraction method is applied, the main peak area S of the crystalline mineral of a sample before heating is measured in advance, and the main peak area S_0 thereof after heated at 1000 °C for 2 hours and then air cooled at a cooling rate of 1 to 10 °C / min is also measured. Then, the vitrification ratio χ is calculated using the values of S_0 and S according to the following formula:

$$\text{Vitrification rate } \chi (\%) = 100 \times (1 - S / S_0)$$

[0021] The particle diameter of the calcium aluminate may preferably be 3000 cm² / g or more, more preferably be 4000 cm² / g or more in terms of Blaine specific surface area value, from the viewpoint of initial strength development. If the Blaine specific surface area value is less than 3000 cm² / g, the initial strength development might decrease.

[0022] The usage content of the calcium aluminate may preferably be 1 part or more and 20 parts or less, and may more preferably be 2 parts or more and 10 parts or less, with respect to 100 parts of cement. If the content of the calcium aluminate exceeds 20 parts, the hardening time is too short that water might not penetrate into the solidified body, and if it is less than 1 part, it is difficult to be uniformly mixed with cement, which might result in poor hardening.

[0023] The aggregate contained in the cement composition may include river sand, sea sand, crushed sand, silica sand, and lightweight aggregates, which are commonly used, and one or more of them can be used in combination. When the aggregate is used in a premix product, the dried aggregate may preferably be used.

[0024] The aggregate has a particle diameter of 2.5 mm or more at a rate of 30% or more, and preferably 40% or more and less than 90%. If the aggregate has a particle diameter of 2.5 mm or more at a rate of less than 30%, poor water permeability into the materials might be incurred.

[0025] The usage content of the aggregate may preferably be 100 parts or more and 500 parts or less with respect to 100 parts of the total content of cement and calcium aluminate. If the content is less than 100 parts, the water permeability into the materials

might be lower, and if the content exceeds 500 parts, which might result in the insufficient strength or poor workability.

[0026] A setting modifier with a carboxylic acid structure preferably has a structure in which a part of the hydrocarbon (C_mH_n) structure is substituted with a carboxylic acid or a carboxylate and has a total molecular weight of 1000 or less. It may specifically include citric acid, tartaric acid, succinic acid, lactic acid, and gluconic acid. Alkali salt of the carboxylic acid may include sodium salt, potassium salt, and calcium salt. Among these, tartaric acid and citric acid may preferably be used from the viewpoint of strength development.

[0027] The usage content of the setting modifier with a carboxylic acid structure in the cement composition may preferably be 0.05 part or more and 2 parts or less with respect to 100 parts of the total content of cement and calcium aluminate. If it is less than 0.05 parts, the water permeability into the materials might be lower, if it exceeds 2 parts, which might result in the insufficient strength or poor workability.

[0028] An alkali metal inorganic salt as the setting modifier may include an inorganic salt having lithium, sodium or potassium as a cation and hydroxide, chloride, bromide, carbonic acid, nitric acid, nitrous acid, sulfuric acid, or acetic acid as an anion, and one or more can be used in combination. Among these, lithium carbonate, sodium carbonate, potassium carbonate, lithium chloride, sodium chloride, potassium chloride, lithium nitrate, sodium nitrate, and potassium nitrate may be preferably used from the viewpoint of strength development.

[0029] The usage content of the alkali metal inorganic salt as the setting modifier is not particularly limited, but may preferably be 0.05 part or more and 1 part or less, and may more preferably be 0.1 part or more and 0.5 part or less with respect to 100 parts of the total content of cement and calcium aluminate. When the usage content of the cement additive is less than 0.05 parts or more than 1 part, the effects of the present invention might not be sufficiently obtained.

[0030] The polysaccharide gum may include dutan gum, welan gum, rhamzan gum, gellan gum, xanthan gum, alginic acid gum, carrageenan gum and locust bean gum, and dutantan gum and welan gum may be preferably used.

[0031] The usage content of the polysaccharide gum in the cement composition may preferably be 0.1 part or more and 2 parts or less with respect to 100 parts of the total content of cement and calcium aluminate. If it is less than 0.1 parts, mixing failure might be incurred, and if it exceeds 2 parts, poor workability might be incurred.

[0032] The cement composition according to the embodiment of the present invention may use one or more admixtures of the group consisting an expansion material, a water reducing agent, an AE water reducing agent, a high performance water reducing agent, a high performance AE water reducing agent, foaming agent, thickener, rust inhibitor, antifreeze agent, shrinkage reducing agent, clay minerals such as bentonite, anion exchanger such as hydrotalcite, slag such as granulated blast furnace slag fine powder or air cooled blast furnace slag fine powder, or fine limestone powder in a range that does not substantially impair the object of the present invention, besides the cement, calcium aluminate, aggregate, and setting modifier.

[0033] The cement composition according to the embodiment of the present invention may be partially or wholly pre-mixed. As a mixing apparatus for pre-mixing, an existing mixing apparatus, such as a tilting cylinder mixer, an omni mixer, a Henschel mixer, a V-type mixer, a pro-shear mixer, and a Nauta mixer, can be used.

[0034] The cement composition which is not required to be mixed according to the embodiment of the present invention can be used by filling into a target portion, and watering if needed. As specific method, 70 parts or less of water with respect to 100 parts of the total content of cement and calcium aluminate in the cement composition of the present invention is put into construction target portion such as road surface and slope, then, the cement composition is filled in the target portion, and if necessary, 5 parts or more and 50 parts or less of water are sprinkled with respect to 100 parts of the total content of cement and calcium aluminate. Watering on the both upper and lower surfaces of the cement composition according to the present invention is not required, but it is desirable to watering on the both surfaces for the viewpoint of suppressing material scattering and dust generation.

[0035] Hereinafter, the present invention will be described in detail based on examples.

EXAMPLES

[0036] [Experiment 1]

10 parts of calcium aluminate and 400 parts by mass of aggregate were mixed with 100 parts of ordinary Portland cement by a Nauta mixer, and a cement composition was prepared without adding gypsum.

100 ml of water was put in a cylindrical container having a diameter of 10 cm and a height of 50 cm, 1000 g of the cement composition was put thereon, the surface was quickly flattened, 50 ml of water was sprinkled over the surface with a watering to be hardened. The mold was removed after 3 minutes from sprinkling, and compressive strength and water penetration rate were immediately measured.

Compressive strength: the upper and lower surfaces of the hardened body after demolding were flattened, and a compression test was conducted accordance with JIS A 1108: 2006.

Water permeability ratio: the hardened body was cut into half through the center part from the upper to the lower surface and the water permeability ratio was calculated from the following formula.

Water permeation ratio (%) = ((Diameter of the hardened body – Diameter of non-water penetrating portion) / (Diameter of the hardened body)) × 100 = ((10–Diameter of non-water penetrating portion) / 10) × 100

[0037] <Materials used>

Cement: Ordinary Portland cement, Blaine specific surface area value 3210 cm² / g, manufactured by Denka Corporation.

Calcium aluminate: limestone and bauxite as raw materials were mixed with the rate of 1.0 to 3.0 of the C / A molar ratio, melted in an electric furnace at 1700 °C for 1 hour, rapidly cooled and vitrified (all vitrification rate were 95%). Then, it was grind and pulverized to be adjusted to the brain specific surface area value 3000, 4000, and 5000cm² / g.

Aggregate: River sand (Himekawa, Niigata Prefecture) with 2.64 specific gravity was dried and adjusted the diameter size.

Dutan gum: manufactured by Sansho Co., Ltd.

[0038] [Table 1]

Experiment No.	Calcium aluminate		Aggregate Percentage (%)					Properties after 3 minutes of watering		Remarks
	C/A molar ratio	Brain specific surface area (cm2/g)	Aggregate Particle Diameter (mm)					Water permeation ratio (%)	Compressive strength (N/mm2)	
			>5	>2.5	>1.2	>0.6	>0.3			
1-1	1.0	4000	30	15	15	10	30	97	0.1	Example
1-2	2.0							86	0.9	Example
1-3	3.0							72	1.3	Example
1-4	2.0	3000	15	30	25	10	20	90	0.4	Example
1-5		5000						82	1.1	Example
1-6	2.0	4000						15	15	30
1-7			0	30				82	0.9	Example
1-8			0	40	25	10	25	85	0.9	Example
1-9			0	50	20	10	20	88	1.1	Example
1-10			0	60	10	10	20	88	1.3	Example
1-11			0	100	0	0	0	99	0.1	Example
1-12	2.0	4000	0	0	0	20	80	30	N.D.*1	Comparative Example
1-13			0	0	0	50	50	50	N.D.*1	Comparative Example
1-14			40	40	0	0	20	93	1.1	Example
1-15			40	40	0	0	20	91	1.3	Example*2

*1 N.D.:Not Detectable

*2 1 part by mass of Dutan gum was added with respect to 100 parts by mass of cement and calcium aluminate.

[0039] As shown in Table 1, when the cement composition according to the embodiment of the present invention was used, water could penetrate into the cement composition without mixing within 3 minutes after watering, and the strength required for maintaining the shape could be obtained. On the other hand, in the case of the Experiments 1-12 and 1-13 using only fine aggregate, the water permeability ratio was too low, and the compressive strength could not be measured. In addition, Experiment 1-15 in which dutan gum was added could obtain higher compressive strength compared with Experiment 1-14 which had a similar condition with Experiment 1-15, but dutan gum was not added.

[0040] [Experiment 2]

Experiment 2 was carried out in the same manner as in Experiment 1-2 of Example 1, except that the setting modifier and the polysaccharide gum were used, and the used content of the setting modifier and the polysaccharide gum were changed as shown in Table 2. The results are shown in Table 2.

[0041] <Materials used>

Setting modifier 1

L-tartaric acid: manufactured by Kanto Chemical Co., Inc.

Citric acid: manufactured by Kanto Chemical Co., Inc.

Setting modifier 2

Lithium carbonate: manufactured by Kanto Chemical Co., Inc.

Sodium chloride: manufactured by Kanto Chemical Co., Inc.

Potassium nitrate: manufactured by Kanto Chemical Co., Inc.

Potassium sulfate: manufactured by Kanto Chemical Co., Inc.

Polysaccharide gum

Welan gum: manufactured by San-Ei Gen F.F.I., Inc.

Dutan gum: manufactured by Sansho Co., Ltd.

Experiment No.	Setting modifier 1		Setting modifier 2		Polysaccharide gum		Properties after 3 minutes of watering		Remarks
	Materials	Added Amount (Parts)	Materials	Added Amount (Parts)	Materials	Added Amount (Parts)	Water permeation ratio (%)	Compressive strength (N/mm ²)	
1-2	-	0	-	0	-	0	86	0.9	Example
2-1	L-tartaric acid	0.5	-	0	-	0	90	0.6	Example
2-2	L-tartaric acid	0.1	Lithium carbonate	0.1	-	0	85	1.1	Example
2-3	L-tartaric acid	0.5	Lithium carbonate	0.1	-	0	90	1.1	Example
2-4	L-tartaric acid	1	Lithium carbonate	0.1	-	0	95	1.2	Example
2-5	L-tartaric acid	0.5	Sodium chloride	0.1	-	0	84	0.9	Example
2-6	Citric acid	0.5	Potassium nitrate	0.1	-	0	93	1.0	Example
2-7	L-tartaric acid	0.5	Potassium sulfate	0.1	Welan gum	0.1	91	1	Example
2-8	L-tartaric acid	0.5	Potassium sulfate	0.1	Welan gum	1	95	0.9	Example
2-9	L-tartaric acid	0.5	Potassium sulfate	0.1	Welan gum	2	96	0.8	Example
2-10	L-tartaric acid	0.5	Potassium sulfate	0.1	Dutan gum	1	95	0.9	Example

The added amount of setting modifier is based on 100 parts of the total of cement and calcium aluminate.

The added amount of polysaccharide gum is based on 100 parts of the total of cement and calcium aluminate.

[0043] As shown in Table 2, when the setting modifier and the polysaccharide gum were used in combination with the cement composition according to the embodiment of the present invention, the water permeability was higher for maintaining the performance, and the compressive strength was equal to or higher than those without adding the setting modifier and the polysaccharide gum.

[0044] When the cement composition according to the embodiment of the present invention was used, water could penetrate into the cement composition without mixing within 3 minutes after watering, and the strength required for maintaining the shape was obtained.

[0045] [Experiment 3]

Experiment 3 was carried out in the same manner as in Experiment 1-2 of Example 1 and Experiment 2-1 of Example 2, except that the used content of the calcium aluminate and the setting modifier was added. The results are shown in Table 3.

[0046] [Table 3]

Experiment No.	Calcium aluminate	Setting modifier		Properties after 3 minutes of watering		Remarks
		Materials	Added Amount (Parts)	Water permeation ratio (%)	Compressive strength (N/mm ²)	
1-2	10	-	0	86	0.9	Example
2-1		L-tartaric acid	2	90	0.6	Example
3-1	1	-	0	100	0.1	Example
3-2	2	-	0	100	0.2	Example
3-3	20	-	0	75	0.8	Example
3-4	20	L-tartaric acid	2	80	1.0	Example

The added amount of calcium aluminate is added based on 100 parts of cement.
The added amount of setting modifier is added based on 100 parts of the total of cement and calcium aluminate.

[0047] As shown in Table 3, when the content of calcium aluminate and the setting modifier contained in the cement composition according to an embodiment of the present invention were adjusted, the water permeability was improved for maintaining the performance, and the compressive strength was equal to or higher.

[0048] The cement composition according to the embodiment of the present invention allows water penetratation into the cement composition without mixing within 3 minutes after watering, and also provides the strength required for maintaining the shape.

CLAIMS

1. A cement composition which is not required to be mixed, comprising:
cement;
calcium aluminate; and
aggregate,
wherein the calcium aluminate has 1.0 or more and 3.0 or less of a $\text{CaO} / \text{Al}_2\text{O}_3$ molar ratio, and
wherein the aggregate has a particle diameter of 2.5 mm or more at a rate of 30% or more.
2. The cement composition which is not required to be mixed according to Claim 1, further comprising a setting modifier with a carboxylic acid structure.
3. The cement composition which is not required to be mixed according to Claim 1 or 2, further comprising an alkali metal inorganic salt as a setting modifier.
4. The cement composition which is not required to be mixed according to any one of Claims 1 to 3, further comprising polysaccharide gum.
5. A construction method, comprising:
filling a target portion with the cement composition which is not required to be mixed according to any one of Claims 1 to 4; and
watering over the filled cement composition.
6. A method for producing a cement composition which is not required to be mixed, the method comprising:
mixing, without an addition of gypsum, cement, calcium aluminate with 1.0 or more and 3.0 or less of a $\text{CaO} / \text{Al}_2\text{O}_3$ molar ratio, and an aggregate having a particle diameter of 2.5 mm or more at a rate of 30% or more.