

DESCRIPTION

Title of Invention

CEMENT COMPOSITION AND METHOD FOR PRODUCING SAME

5

Technical Field

[0001]

The present invention relates to a cement composition and a method for producing the same.

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Background Art

[0002]

Various studies have been made to improve the strength of mortar and concrete.

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For example, in Patent Literature No. 1, in order to provide admixtures or cement compositions for mortar or concrete used in civil engineering structures or concrete secondary products that have the effect of increasing both 7-day strength and 28-day strength, an admixture containing trialkanolamine and diethylene glycol, and a cement composition containing cement and the admixture is disclosed.

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In addition, for example, in Patent Literature No. 2, in manufacturing buildings, civil engineering structures, and concrete secondary products, in order to provide cement

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admixtures and cement compositions improved to be able to

overcome the drawback of low initial strength of fly ash and actively blend fly ash with cement to be used, a cement composition containing cement admixture that contains fly ash, trialkanolamine, and 0.05 to 0.5 parts by weight of diethylene glycol with respect to 100 parts by weight of fly ash or a cement admixture containing cement, diethylene glycol, and trialkanolamine, and furthermore, a cement composition containing cement, fly ash, trialkanolamine, and diethylene glycol are disclosed.

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Citation List

Patent Literature

[0003]

[Patent Literature No. 1] Japanese Laid-open Patent

15 Publication No. 2000-203909

[Patent Literature No. 2] Japanese Laid-open Patent

Publication No. 2000-281404

Summary of Invention

20 Technical Problem

[0004]

However, flowability of the cement compositions described in Patent Literature No. 1 and Patent Literature No. 2 has not been studied.

25 An object of the present invention is to provide a cement

composition having high strength and excellent flowability, and a method for producing the same.

Solution to Problem

5 [0005]

The present invention provides the following <1> to <7>.

<1> A cement composition containing: an ordinary Portland cement clinker containing 51% to 62% by mass of C_3S and 7% to 10% by mass of C_4AF , which are calculated by Bogue's formula;
10 a gypsum; a limestone; and an auxiliary agent containing alkanolamine, in which a content of the alkanolamine in a total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 10 to 210 mg/kg, a content of the limestone in a total amount of the ordinary Portland cement clinker, the
15 gypsum, the auxiliary agent, and the limestone is 3% to 10% by mass, a unit cell volume of C_4AF is more than 0.4290 nm^3 , and Blaine specific surface area is 2,800 to 3,500 cm^2/g .

[0006]

<2> The cement composition according to <1>, in which a
20 content of the auxiliary agent in the total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 80 to 350 mg/kg.

<3> The cement composition according to <1> or <2>, in which the auxiliary agent contains an aliphatic polyhydric
25 alcohol.

<4> The cement composition according to any one of <1> to <3>, in which a content of the gypsum in the total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 0.7% to 2.8% by mass in terms of SO_3 .

5 <5> The cement composition according to any one of <1> to <4>, in which the alkanolamine is at least one selected from the group consisting of diethanolisopropanolamine, triisopropanolamine, ethanoldiisopropanolamine, N-methyldiethanolamine, and Nn-butyldiethanolamine.

10 <6> The cement composition according to any one of <3> to <5>, in which the aliphatic polyhydric alcohol is at least one selected from the group consisting of glycerin and diethylene glycol.

[0007]

15 <7> A method for producing a cement composition including: producing the cement composition according to any one of <1> to <6> by mixing an ordinary Portland cement clinker that contains 51% to 62% by mass of C_3S and 7% to 10% by mass of C_4AF , which are calculated by Bogue's formula, and that has a unit
20 cell volume of C_4AF of more than 0.4290 nm^3 , a gypsum, a limestone, and an auxiliary agent containing alkanolamine such that a blending amount of the alkanolamine in a total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 10 to 210 mg/kg and a blending amount of the limestone
25 in a total amount of the ordinary Portland cement clinker, the

gypsum, the auxiliary agent, and the limestone is 3% to 10% by mass.

Advantageous Effects of Invention

5 [0008]

According to the present invention, it is possible to provide a cement composition having high strength and excellent flowability, and a method for producing the same.

10 Description of Embodiments

[0009]

The notation of a numerical range from "AA to BB" in the present specification means "equal to or higher than AA and equal to or lower than BB".

15 [0010]

<Cement Composition>

A cement composition of the present invention contains an ordinary Portland cement clinker containing 51% to 62% by mass of C_3S and 7% to 10% by mass of C_4AF , which are calculated by Bogue's formula, a gypsum, a limestone, and an auxiliary agent containing alkanolamine, in which a content of the alkanolamine in a total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 10 to 210 mg/kg, a content of the limestone in a total amount of the ordinary Portland cement
25 clinker, the gypsum, the auxiliary agent, and the limestone is

3% to 10% by mass, a unit cell volume of C_4AF is more than 0.4290 nm^3 , and Blaine specific surface area is 2,800 to 3,500 cm^2/g .

[0011]

A cement composition is usually obtained by calcinating
5 blended raw materials in a rotary kiln to obtain clinker, adding
gypsum and limestone to the obtained clinker, and pulverizing
those materials by a finishing mill until a desired Blaine
specific surface area is achieved.

In a case of pulverizing cement by the finishing mill, it
10 is common practice to add a dispersant such as diethylene glycol
to products to be pulverized, thereby preventing a decrease in
pulverization efficiency caused by agglomeration of particles.
Strength development, which is a major physical property of
ordinary Portland cement, is generally controlled by adjusting
15 raw material blending and cement fineness (Blaine specific
surface area). The Blaine specific surface area of the cement
composition is adjusted in the pulverization step by the
finishing mill, and is a factor controlling the strength level
at each material age, so that the Blaine specific surface area
20 is regarded as a quality control item.

[0012]

In a case where the Blaine specific surface area increases,
the initial strength of mortar and concrete increases in
particular, but the flowability during kneading of cement paste
25 is reduced, which causes the reduction of work efficiency. In

a case where the amount of chemical admixture is increased to maintain flowability, the cost is increased, and in a case where the amount of water is increased, drying and shrinkage of a cured product are increased, resulting in promoting cracking of the
5 cured product and impairing durability.

[0013]

In a case where cement is stored in a silo, the higher the Blaine specific surface area, the higher the reactivity of cement particles with moisture, carbon dioxide, and the like in the
10 air. Therefore, the hydration activity of surfaces of the cement particles is lowered, and so-called weathering is likely to occur. Weathered cement causes problems such as abnormal setting after pouring water, reduced flowability, and reduced strength of a cured product.

15 Calcium hydroxide formed on the surfaces of the cement particles by weathering reacts with carbon dioxide to form calcium carbonate, which promotes agglomeration of the cement particles. As a result, lumps are generated in the silo, which also causes a so-called consolidation.

20 [0014]

Therefore, it is preferable to reduce the Blaine specific surface area of the cement composition as much as possible within a range in which the desired strength is obtained. In addition, from the viewpoint of production, it is preferable to reduce
25 the Blaine specific surface area of the cement composition. As

described above, the Blaine specific surface area of the cement composition is adjusted in the pulverization step by the finishing mill, and reducing the Blaine specific surface area leads to power reduction during the operation of the finishing mill.

[0015]

In addition, the strength development can be controlled by adjusting a ratio of limestone in the raw materials, in addition to adjusting the Blaine specific surface area. For example, the ratio of limestone in the raw materials is increased to increase the amount of alite in cement minerals, and particularly the strength development at the initial stage of hydration is increased.

In this way, the amount of limestone in the clinker raw materials can be relatively increased, and the amount of alite in the generated cement minerals can be increased to enhance the strength. However, in a case where the amount of alite increases, the raw materials for cement become difficult to calcinate, thereby the amount of fuel required for calcinating increasing. An increase in a raw material unit consumption of limestone and an increase in the amount of coal used as the main fuel also contribute to an increase in carbon dioxide emissions.

[0016]

On the other hand, the cement composition of the present invention keeps the Blaine specific surface area of the cement

composition low, enhances the strength while suppressing the amount of limestone in the clinker raw materials, and is excellent in flowability. Although the reason for this is not clear, it is presumed to be due to the following reasons.

5 [0017]

Alkanolamine, which is an auxiliary agent contained in the cement composition of the present invention, dissolves specifically a ferrite phase among four minerals of alite, belite, aluminate, and ferrite, which are main cement minerals, thereby
10 enabling the strength of the cement to be enhanced. Specifically, alkanolamine dissolves the ferrite phase present on surfaces of cement particles synthesized from various minerals to increase surface areas of the cement particles, and the cement minerals inside come into contact with water to
15 promote hydration. In addition, iron hydroxide produced by dissolution of ferrite covers surfaces of clinker particles and inhibits the diffusion of Ca ions and the like eluted from clinker minerals such as alite, thereby inhibiting hydration. Thus, it is considered that alkanolamine also has the effect of promoting
20 the hydration of alite because alkanolamine also has the effect of dissolving Fe ions of the iron hydroxide.

The cement composition of the present invention will be described in detail below.

[0018]

25 [Blaine Specific Surface Area]

The cement composition of the present invention has a Blaine specific surface area of 2,800 to 3,500 cm²/g.

In a case where the Blaine specific surface area is lower than 2,800 cm²/g, alkanolamine has a hydration promoting effect, but mortar strength decreases. In a case where the Blaine specific surface area is higher than 3,500 cm²/g, the flowability decreases, and the dissolution of C₄AF by alkanolamine is limited, resulting in a strength enhancement effect cannot be obtained.

From the viewpoint of further enhancing the strength, the Blaine specific surface area of the cement composition is preferably 3,000 to 3,400 cm²/g, and more preferably 3,150 to 3,350 cm²/g.

The Blaine specific surface area of the cement composition may be measured according to JIS R 5201:2015 "Method for Physical Testing of Cement".

[0019]

[Clinker]

The clinker used in the cement composition of the present invention is an ordinary Portland cement clinker containing 51% to 62% by mass of C₃S and 7% to 10% by mass of C₄AF, which are calculated by Bogue's formula.

A total amount of C₃S(3CaO·SiO₂) and C₂S(2CaO·SiO₂) in the clinker is constant at approximately 88% by mass, and in a case where C₃S is 51% to 62% by mass, a content of C₂S is 16% to 27% by mass. In addition, A total amount of C₃A(3CaO·Al₂O₃) and

$C_4AF(4CaO \cdot Al_2O_3 \cdot FeO_3)$ in the clinker is constant at approximately 18.5% by mass, and in a case where C_4AF is 7% to 10% by mass, a content of C_3A is 8.5% to 12.5% by mass.

[0020]

5 (C_3S and C_2S)

In a case where the content of C_3S in the clinker is less than 51% by mass, the mortar strength is not excellent, and even though the mortar strength can be increased, the flowability is not excellent. In addition, the strength enhancement effect
10 obtained by the addition of alkanolamine cannot be expected due to the following reasons.

[0021]

In a case where the content of C_3S in the clinker is less than 51% by mass, a content of C_2S , which has the relatively poor
15 pulverizability, increases. As a result, a pulverization time required to obtain a certain Blaine specific surface area of the cement composition is longer, and minerals other than C_2S (C_3S , C_3A , and C_4AF), which have good pulverizability, over-pulverize to increase the Blaine specific surface area.
20 In addition, an increase in opportunities making C_4AF come into contact with water of adjacent C_4AF is caused by the strength enhancement mechanism by means of adding alkanolamine to promote hydration and enhance the strength by selectively dissolving C_4AF in the clinker. However, in a case where the clinker is
25 over-pulverized, clinker particles in which various minerals

originally exist in combination tend to exist as individual minerals, so that dissolution of C_4AF does not lead to promotion of hydration of C_4AF . Therefore, the strength enhancement effect by the addition of alkanolamine cannot be obtained.

5 [0022]

In a case where the content of C_3S in the clinker is more than 62% by mass, the raw materials for cement become difficult to calcinate, unreacted lime (f. CaO) increases, and the amount of fuel consumption increases in the production of the clinker, which are not preferable.

From the viewpoint of enhancing the strength and flowability and suppressing the amount of fuel consumption, the content of C_3S in the clinker is preferably 53% to 61% by mass, and more preferably 55% to 59% by mass.

15 [0023]

(C_4AF and C_3A)

In a case where the content of C_4AF in the clinker is less than 7% by mass, the content of C_4AF is too small. Thus, the promotion of a reaction of C_3S by the promotion of dissolution of C_4AF is limited, and a remarkable strength enhancement effect cannot be exhibited, even though alkanolamine is added. In addition, in the efficient production of the clinker, since it is necessary to keep the amount of a liquid phase ($C_3A + C_4AF$) constant, a decrease in C_4AF means a relative increase in C_3A , and in a case where the amount of C_3A increases, the flowability

deteriorates due to the formation of a large amount of needle crystal ettringite produced by a reaction between C_3A and gypsum during initial hydration.

[0024]

5 In a case where the content of C_4AF in the clinker is more than 10% by mass, alkanolamine dissolves C_4AF on surfaces of clinker particles, and the hydration of C_3S is temporarily promoted, but a large amount of iron hydroxide gel produced by the dissolution of Fe ions in C_4AF thickly covers the surfaces
10 of the clinker particles, which causes hydration to be delayed.

From the viewpoint of enhancing the strength and flowability and suppressing the amount of fuel consumption, the content of C_4AF in the clinker is preferably 7% to 9% by mass, and more preferably 8% to 9% by mass.

15 [0025]

[Unit cell volume of C_4AF]

A unit cell volume of C_4AF is higher than 0.4290 nm^3 .

In a case where the unit cell volume of C_4AF is equal to or lower than 0.4290 nm^3 , the solubility of C_4AF by alkanolamine
20 is low. Therefore, the hydration promoting effect of C_3S is not obtained, and the mortar strength is lowered.

The unit cell volume of C_4AF is preferably equal to or higher than 0.4295 nm^3 , and more preferably equal to or higher than 0.4300 nm^3 . Although the upper limit of the unit cell volume
25 of C_4AF is not particularly limited, the upper limit is usually

equal to or lower than 0.4320 nm^3 .

The unit cell volume of C_4AF can be calculated by whole pattern fitting (WPF) analysis from the lattice constant of C_4AF measured by using the Rietveld analysis method with powder X-ray
5 diffraction.

[0026]

[Auxiliary Agent]

The cement composition of the present invention contains an auxiliary agent containing alkanolamine, and a content of
10 alkanolamine in a total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 10 to 210 mg/kg.

The auxiliary agent specifically means a grinding aid, alkanolamine also acts as a strength enhancing agent. The auxiliary agent may contain components other than alkanolamine,
15 and examples thereof include an aliphatic polyhydric alcohol.

In a case where the content of alkanolamine in the cement composition of the present invention is less than 10 mg/kg, a concentration is too low to promote hydration of alite by the dissolution of C_4AF . As a result, the strength enhancement
20 effect cannot be obtained. In a case where the content of alkanolamine in the cement composition of the present invention is higher than 210 mg/kg, the enhancement effect of the initial strength is remarkable. However, at a material age of 28 days, the hydration structure is coarse due to the high initial
25 hydration activity, and as a result, the strength enhancement

effect cannot be obtained.

[0027]

(Alkanolamine)

Examples of alkanolamine include monoethanolamine,
5 diethanolamine, triethanolamine, monoisopropanolamine,
diisopropanolamine, triisopropanolamine, methylethanolamine,
methyldiisopropanolamine, Nn-butylethanolamine,
N-methyldiethanolamine, Nn-butyldiethanolamine,
N-methyldiisopropanolamine, diethanolisopropanolamine,
10 diisopropanolethanolamine, tetrahydroxyethylethylenediamine,
N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine,
tris(2-hydroxybutyl)amine, and other amines.

Only one kind of alkanolamine may be used, or two or more
kinds thereof may be used.

15 [0028]

Among these, alkanolamine is preferably at least one
selected from the group consisting of diethanolisopropanolamine
(DEIPA), triisopropanolamine (TIPA),
ethanoldiisopropanolamine (EDIPA), N-methyldiethanolamine
20 (MDEA), and Nn-butyldiethanolamine (BDEA), more preferably at
least one selected from the group consisting of
diethanolisopropanolamine (DEIPA), triisopropanolamine (TIPA),
and N-methyldiethanolamine (MDEA), and still more preferably
diethanolisopropanolamine (DEIPA).

25 [0029]

(Aliphatic Polyhydric Alcohol)

The auxiliary agent preferably contains an aliphatic polyhydric alcohol.

The aliphatic polyhydric alcohol preferably has 3 to 20
5 carbon atoms, and more preferably 3 to 10 carbon atoms.

The aliphatic polyhydric alcohol preferably has 2 to 8 hydroxyl groups, and more preferably 2 to 4 hydroxyl groups.

The aliphatic polyhydric alcohol preferably has a molecular weight of 70 to 420, and more preferably 70 to 210.

10 [0030]

Specific examples of the aliphatic polyhydric alcohol include glycols such as ethylene glycol, diethylene glycol, and polyethylene glycol; glycerin and the like. Only one kind of the aliphatic polyhydric alcohol may be used, or two or more
15 kinds thereof may be used.

The aliphatic polyhydric alcohol is preferably at least one selected from the group consisting of glycerin and diethylene glycol, and diethylene glycol is more preferably included.

[0031]

20 In addition, a content of the auxiliary agent in the total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is preferably 80 to 350 mg/kg.

Hereinafter, a "total of the auxiliary agents" means the "content of the auxiliary agent in the total amount of the
25 ordinary Portland cement clinker, the gypsum, and the auxiliary

agent".

In a case where the total of the auxiliary agents is equal to or higher than 80 mg/kg, the cement composition is excellent in pulverizability. That is, in a case where the clinker, the gypsum, and the limestone are added and pulverized by a ball-mill, pulverized products are less likely to adhere to a medium, and the inhibition of pulverization is suppressed. In a case where the total of the auxiliary agents is equal to or lower than 350 mg/kg, floodability is excellent. That is, an air-entraining property of kneaded products is suppressed, a decrease in the strength is suppressed, and the flowability of powder does not increase more than necessary. Thus, the cement composition is difficult to slip during transportation on a belt conveyor, conveyance on up-grade is easy, and slipping down on down-grade is prevented due to its own weight. As a result, it is possible to efficiently transport the cement composition.

The total of the auxiliary agents is more preferably 100 to 350 mg/kg, and still more preferably 150 to 300 mg/kg, from the viewpoint of further improving pulverizability and floodability.

[0032]

[Limestone]

The cement composition of the present invention contains limestone.

The limestone has a content of 3% to 10% by mass in the

total amount of the ordinary Portland cement clinker, the gypsum, the auxiliary agent, and the limestone.

Hereinafter, the "content of the limestone" means a "content of the limestone in the total amount of the ordinary Portland cement clinker, the gypsum, the auxiliary agent, and the limestone".

In a case where the content of the limestone is less than 3% by mass, the strength enhancement effect cannot be obtained.

Usually, ettringite, which is produced during the initial hydration, undergoes a reaction of conversion into monosulfate as the hydration of cement proceeds. However, coexistence of the limestone and alkanolamine contributes to the strength enhancement by the promotion of the addition to monocarbonate or hemihydrate. However, in a case where the content of the limestone is less than 3% by mass, the reaction does not occur remarkably, which does not lead to the strength enhancement.

In a case where the content of the limestone is more than 10% by mass, the unit amount of the clinker in the cement decreases, resulting in a decrease in mortar strength.

The content of the limestone is preferably 3% to 9% by mass, and more preferably 4% to 8% by mass, from the viewpoint of further enhancing the strength.

[0033]

[Gypsum]

The cement composition of the present invention contains

gypsum.

A content of the gypsum in the total amount of the ordinary Portland cement clinker, the gypsum, and alkanolamine is preferably 0.7% to 2.8% by mass in terms of SO_3 .

5 Hereinafter, the "content of the gypsum" means a "content of the gypsum in the total amount of the ordinary Portland cement clinker, the gypsum, the alkanolamine".

By setting the content of the gypsum within the above range, the setting time of the cement composition, the flowability after
10 pouring water, and change over time thereof can be appropriately maintained, and the strength development, and drying and shrinkage can be made appropriate as properties after hardening.

From the above viewpoint, the content of the gypsum is more preferably 0.8% to 2.5% by mass, and still more preferably 0.9%
15 to 2.0% by mass in terms of SO_3 .

The content of the gypsum can be measured according to JIS R 5202:2010 "Method for chemical analysis of Portland cement". A mass ratio of the gypsum in the cement composition in terms of SO_3 can be obtained from the amount of the blended gypsum and
20 a ratio of SO_3 contained in the gypsum.

As the gypsum, any one of anhydrous gypsum, hemihydrate gypsum, and dihydrate gypsum can be used.

[0034]

[Other Component]

25 In the cement composition of the present invention, a fly

ash, a blast-furnace slag, a silica fume, or the like can be further added for adjusting flowability, hydration rate, strength development, and the like.

[0035]

5 <Method for Producing Cement Composition>

A method for producing a cement composition of the present invention is a method for producing the cement composition of the present invention by mixing an ordinary Portland cement clinker that contains 51% to 62% by mass of C_3S and 7% to 10%
10 by mass of C_4AF , which are calculated by Bogue's formula, and that has a unit cell volume of C_4AF of more than 0.4290 nm^3 , a gypsum, a limestone, and an auxiliary agent containing alkanolamine such that a blending amount of the alkanolamine in a total amount of the ordinary Portland cement clinker, the
15 gypsum, and the auxiliary agent is 10 to 210 mg/kg and a blending amount of the limestone in a total amount of the ordinary Portland cement clinker, the gypsum, the auxiliary agent, and the limestone is 3% to 10% by mass.

The blending amount of the alkanolamine is the same as the
20 content of the alkanolamine in the cement composition of the present invention, and the preferred range is also the same. In addition, the blending amount of the limestone is synonymous with the content of the limestone described above, and the preferred range is also the same.

25 [0036]

The order, timing, and other conditions of adding the auxiliary agent, the gypsum, and the limestone to the clinker are not particularly limited. For example, the gypsum and the limestone may be added to the clinker and mixed, and the auxiliary agent may be then added and mixed, or the auxiliary agent may be added to the clinker, and the gypsum and the limestone may be then added.

[0037]

The means for mixing each component in the method for producing a cement composition of the present invention is not particularly limited. Examples thereof include mixers, ball-mills, roche-mills, and air-blending silos. The mixing time can be set within a range in which it is determined that sufficient mixing is carried out in the normal production of a cement composition.

[0038]

In the present production method, pulverization is preferably carried out so that the Blaine specific surface area of the cement composition is 2,800 to 3,500 cm²/g.

20 [0039]

In the method for producing a cement composition of the present invention, a blast-furnace slag, a siliceous admixture, and a fly ash can be further added in addition to adding the ordinary Portland cement clinker, the gypsum, the limestone, and the auxiliary agent containing alkanolamine.

In the present invention, the blast-furnace slag and siliceous admixture defined in JIS R 5210:2009 "Portland cement" can be used. Regarding the fly ash, in addition to the fly ash type I and fly ash type II defined in JIS R 5210:2009 "Portland cement", the fly ash type III and fly ash type IV can also be used.

Examples

[0040]

The present invention will be described in more detail below with reference to Examples. The present invention is not limited to the following Examples.

[0041]

<Production of Cement Composition>

The following materials were used in the production of cement compositions.

1. Clinker

Seven types of A to G ordinary Portland cement clinkers (manufactured by SUMITOMO OSAKA CEMENT Co., Ltd.) were used. Chemical compositions and mineral compositions are shown in Table 1. The chemical composition of the clinker was analyzed by the glass beads method by using a fluorescent X-ray measuring device (PRIMUS IV, manufactured by Rigaku Corporation) in accordance with JIS R 5204:2019 "Method for fluorescent X-ray analysis of cement". The mineral compositions were calculated by using Bogue's formula from the obtained mass ratios of CaO,

SiO₂, Al₂O₃, and Fe₂O₃. In Table 1, HM means the hydraulic modulus, SM means the silica modulus, and IM means the iron modulus.

$$C_3S = (4.07 \times CaO) - (7.60 \times SiO_2) - (6.72 \times Al_2O_3) - (1.43 \times Fe_2O_3)$$

$$5 \quad C_2S = (2.87 \times SiO_2) - (0.754 \times C_3S)$$

$$C_3A = (2.65 \times Al_2O_3) - (1.69 \times Fe_2O_3)$$

$$C_4AF = 3.04 \times Fe_2O_3$$

[0042]

"Unit cell volume of C₄AF" in Table 1 is calculated by WPF
 10 analysis from a lattice constant of C₄AF measured by using the Rietveld analysis method with powder X-ray diffraction.

(Measurement Condition)

· Powder X-ray diffractometer: X7Pert PRO manufactured by Malvern Panalytical Ltd.

15 · Rietveld analysis software: High Score Plus manufactured by Malvern Panalytical Ltd.

· X-ray tube bulb: Cu (tube voltage: 45 kV, tube electric current: 40 mA)

· Slit: divergence slit-variable (irradiation width-12mm,
 20 Antiscatter slit-2°)

· Measurement range: 10° to 70° (step width: 0.0167°)

· Scanning speed: 0.1013°/s

[0043]

[Table 1]

Clinker type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂
	%	%	%	%	%	%	%	%	%	%
A	22.31	5.40	2.79	65.10	1.79	0.53	0.28	0.47	0.19	0.42
B	22.12	5.70	2.25	65.63	1.81	0.50	0.28	0.46	0.18	0.42
C	22.75	5.40	2.79	64.79	1.81	0.50	0.28	0.46	0.18	0.42
D	22.02	5.18	3.24	65.30	1.83	0.50	0.28	0.45	0.19	0.42
E	21.74	5.40	2.79	65.60	1.90	0.50	0.28	0.45	0.19	0.42
F	22.53	5.10	3.39	64.70	1.83	0.50	0.28	0.45	0.19	0.42
G	22.28	5.43	2.77	65.26	1.79	0.53	0.28	0.47	0.19	0.42
Clinker type	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	f. CaO	C ₄ AF Unit cell volume	HM	SM	IM	
	%	%	%	%	%	nm ³	%	%	%	
A	55.1	22.5	8.5	9.6	0.6	0.4302	2.13	2.72	1.94	
B	57.5	20.1	6.8	11.3	0.7	0.4298	2.18	2.78	2.53	
C	50.5	27.2	8.5	9.6	0.5	0.4308	2.09	2.78	1.94	
D	59.0	18.7	9.8	8.3	0.8	0.4293	2.15	2.62	1.60	
E	61.5	16.0	8.5	9.6	1.2	0.4296	2.19	2.65	1.94	
F	53.0	24.7	10.3	7.8	0.5	0.4301	2.09	2.65	1.50	
G	55.8	21.8	8.4	9.7	0.5	0.4286	2.14	2.72	1.96	

[0044]

2. Auxiliary Agent

(1) Alkanolamine

· DEIPA: Diethanolisopropanolamine [manufactured by
5 Tokyo Chemical Industry Co., Ltd.]

· TIPA: Triisopropanolamine [manufactured by Tokyo
Chemical Industry Co., Ltd.]

· EDIPA: Ethanol-diisopropanolamine

[Manufactured by Sigma-Aldrich Japan K.K.]

10 · MDEA: N-methyldiethanolamine [manufactured by Tokyo
Chemical Industry Co., Ltd.]

· BDEA: Nn-butyldiethanolamine [manufactured by Tokyo
Chemical Industry Co., Ltd.]

(2) Aliphatic Polyhydric Alcohol

15 · DEG: Diethylene glycol [manufactured by KANTO KAGAKU.]

[0045]

3. Limestone

Calcium carbonate, special grade, manufactured by KANTO
KAGAKU., CaCO_3 : 99.5%

20 4. Gypsum

Hemihydrate gypsum was used. Specifically, calcium
sulfate dihydrate, grade 1, manufactured by FUJIFILM Wako Pure
Chemical Corporation, CaSO_4 of 98.0+% held for 12 hours at 120°C
in a dryer was used. The gypsum in terms of SO_3 was measured
25 according to JIS R 5202:2015 "Method for chemical analysis of

cement".

[0046]

[Example 1]

2.7% by mass of hemihydrate gypsum (1.5% by mass in terms
5 of hemihydrate gypsum SO_3) and 4.5% by mass of limestone were
added to 92.8% by mass(*) of a clinker that is a type A clinker,
and mixed by a mixer. Next, as shown in Table 2, each of
diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG)
was blended by 10 mg/kg and 190 mg/kg, as auxiliary agents, to
10 a total amount of the clinker, the gypsum, and the auxiliary
agents. Next, mixing and pulverizing were carried out with a
ball-mill so that the Blaine specific surface area value was
in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement
composition of Example 1.

15 Regarding the amount with (*), a total of the clinker and
the auxiliary agent is 92.8% by mass, but the amount of the
auxiliary agent is an extremely small amount that hardly affects
the amount of the clinker when considered as a percentage of
the total of the clinker and the auxiliary agent, and it can
20 be said that the amount of the clinker is 92.8% by mass. The
same applies to Examples other than Example 1 and Comparative
Examples.

[0047]

Regarding the blending amount of the gypsum, since the
25 gypsum in terms of SO_3 acts on the clinker, hemihydrate gypsum

was blended so that the hemihydrate gypsum in terms of SO_3 /(a total amount of the clinker + the auxiliary agent + the hemihydrate gypsum) was 1.5% in all of Examples and Comparative Examples.

5 [0048]

[Examples 2 to 19, and 23 to 26, and Comparative Examples 1 to 4, and 7 to 12]

Cement compositions were obtained in the same manner as in Example 1, except that clinkers having the types shown in
10 Tables 2 and 3 were used as the clinker, the limestone was blended in the amount shown in Tables 2 and 3, and auxiliary agents [alkanolamine, and optionally an aliphatic polyhydric alcohol (DEG)] having the types and amounts of the column "Auxiliary agent" shown in Tables 2 and 3, were blended as the auxiliary
15 agent, and those materials were mixed and pulverized by a ball-mill so that the Blaine specific surface area values were within a range of $\pm 50 \text{ cm}^2/\text{g}$ shown in Tables 2 and 3.

In Comparative Examples 1 and 2, alkanolamine was not blended. In addition, in Comparative Example 2 and the like
20 where the numerical value in the column of "DEG" is 0, diethylene glycol was not blended.

[0049]

[Comparative Example 5]

2.8% by mass of hemihydrate gypsum (1.5% by mass in terms
25 of hemihydrate gypsum SO_3) and 1.0% by mass of limestone were

added to 96.2% by mass of a clinker that is a type A clinker,
and mixed by a mixer. Next, as shown in Table 3, each of
diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG)
was blended by 50 mg/kg and 150 mg/kg, as auxiliary agents, to
5 a total amount of the clinker, the gypsum, and the auxiliary
agents. Next, mixing and pulverizing were carried out with a
ball-mill so that the Blaine specific surface area value was
in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement
composition of Comparative Example 5.

10 [0050]

[Example 20]

2.7% by mass of hemihydrate gypsum (1.5% by mass in terms
of hemihydrate gypsum SO_3) and 3.2% by mass of limestone were
added to 94.1% by mass of a clinker that is a type A clinker,
15 and mixed by a mixer. Next, as shown in Table 3, each of
diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG)
was blended by 50 mg/kg and 150 mg/kg, as auxiliary agents, to
a total amount of the clinker, the gypsum, and the auxiliary
agents. Next, mixing and pulverizing were carried out with a
20 ball-mill so that the Blaine specific surface area value was
in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement
composition of Example 20.

[0051]

[Example 21]

25 2.6% by mass of hemihydrate gypsum (1.5% by mass in terms

of hemihydrate gypsum SO_3) and 6.5% by mass of limestone were added to 90.9% by mass of a clinker that is a type A clinker, and mixed by a mixer. Next, as shown in Table 3, each of diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG) was blended by 50 mg/kg and 150 mg/kg, as auxiliary agents, to a total amount of the clinker, the gypsum, and the auxiliary agents. Next, mixing and pulverizing were carried out with a ball-mill so that the Blaine specific surface area value was in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement composition of Example 21.

[0052]

[Example 22]

2.5% by mass of hemihydrate gypsum (1.5% by mass in terms of hemihydrate gypsum SO_3) and 9.5% by mass of limestone were added to 88.0% by mass of a clinker that is a type A clinker, and mixed by a mixer. Next, as shown in Table 3, each of diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG) was blended by 50 mg/kg and 150 mg/kg, as auxiliary agents, to a total amount of the clinker, the gypsum, and the auxiliary agents. Next, mixing and pulverizing were carried out with a ball-mill so that the Blaine specific surface area value was in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement composition of Example 22.

[0053]

[Comparative Example 6]

2.5% by mass of hemihydrate gypsum (1.5% by mass in terms of hemihydrate gypsum SO_3) and 11.0% by mass of limestone were added to 86.5% by mass of a clinker that is a type A clinker, and mixed by a mixer. Next, as shown in Table 3, each of
5 diethanolisopropanolamine (DEIPA) and diethylene glycol (DEG) was blended by 50 mg/kg and 150 mg/kg, as auxiliary agents, to a total amount of the clinker, the gypsum, and the auxiliary agents. Next, mixing and pulverizing were carried out with a ball-mill so that the Blaine specific surface area value was
10 in a range of $3,200 \pm 50 \text{ cm}^2/\text{g}$, thereby obtaining a cement composition of Comparative Example 6.

[0054]

<Evaluation of Cement Composition>

1. Pulverizability

15 10 kg of high chromium balls with $\phi 9.5 \text{ mm}$ were charged, as pulverizing media, into a ball-mill with $\phi 0.4 \text{ m} \times 0.72 \text{ m}$ (volume of about 90 L), and the cement compositions of Examples and Comparative Examples were added as products to be pulverized. A mill rotation speed was set to 60 times/min, and a pulverization
20 time was measured until the Blaine specific surface area reached $3,200 \text{ cm}^2/\text{g}$.

The shorter the pulverization time, the more excellent the pulverizability of the cement composition. The pulverization time is preferably lower than 68 minutes. The results are shown
25 in the column of "Pulverization effect" shown in Tables 2 and

3.

[0055]

2. Floodability

A repose angle, collapse angle, and dispersion degree of
5 the cement compositions of Examples and Comparative Examples
were measured by using a powder tester (TP-X) manufactured by
Hosokawa Micron Powder Systems. to apply the measurement results
to a floodability index table of the tester, thereby obtaining
a floodability index.

10 The lower the floodability index, the more excellent the
cement composition is in the floodability. The index is
preferably lower than 75. The results are shown in the column
of "Floodability index" of Tables 2 and 3.

[0056]

15 3. Mortar Strength

The strength of each of mortars obtained by using the
cements of Examples and Comparative Examples was evaluated
according to JIS R 5201 "Method for Physical Testing of Cement".

The higher the numerical value, the higher the strength
20 of the mortar obtained by using the cement composition, and the
tolerance is higher than 60 N/mm². The results are shown in the
column of "Mortar strength" of Tables 2 and 3.

[0057]

4. Flowability

25 The flowability of each of the mortars obtained from the

cement compositions was evaluated according to JIS R 5201 "Method for Physical Testing of Cement".

Specifically, 1.0% of a high-performance water reducing agent [manufactured by Kao Corporation, trade name "Mighty 150"]
5 was added to the cement compositions of Examples and Comparative Examples to prepare mortars, and a flow value of each of the obtained mortars was measured when each mortar stopped spreading after a cone was removed without performing 15 falling motions.

The higher the flow value, the more excellent the
10 flowability of the mortar obtained from the cement composition. The tolerance is higher than 160 mm. The results are shown in the column of "0 stroke flow" of Tables 2 and 3.

[0058]

[Table 2]

	Blaine value	Clinker type	Limestone	Auxiliary agent mg/kg						Total of amine	Total of auxiliary agent	Pulverization effect		Floodability index		Mortar strength		0 stroke flow	
	Amine					DEG	28 days												
	cm ² /g			%	DEIPA		TIPA	EDIPA	MDEA							BDEA	mg/kg		
Comparative Example 1	3200	A	4.5	0	0	0	0	0	200	0	200	61	O	63	O	59.2	X	196	
Comparative Example 2	3200	A	4.5	0	0	0	0	0	0	0	0	90	X	48	O	58.8	X	196	O
Comparative Example 3	3200	A	4.5	8	0	0	0	0	192	8	200	61	O	63	O	59.5	X	196	O
Example 1	3200	A	4.5	10	0	0	0	0	190	10	200	60	O	63	O	63.8	O	198	O
Example 2	3200	A	4.5	50	0	0	0	0	150	50	200	59	O	62	O	65.9	O	195	O
Example 3	3200	A	4.5	15	0	0	0	0	60	15	75	71	X	63	O	64.8	O	198	O
Example 4	3200	A	4.5	50	0	0	50	0	50	100	150	67	O	55	O	66.0	O	193	O
Example 5	3200	A	4.5	50	0	0	0	0	40	50	90	67	O	50	O	65.8	O	195	O
Example 6	3200	A	4.5	150	0	0	0	0	150	150	300	59	O	73	O	66.4	O	197	O
Example 7	3200	A	4.5	200	0	0	0	0	140	200	340	59	O	74	O	66.3	O	198	O
Example 8	3200	A	4.5	190	0	0	0	0	0	190	190	61	O	63	O	65.3	O	198	O
Example 9	3200	A	4.5	190	0	0	0	0	60	190	250	60	O	66	O	67.1	O	201	O
Example 10	3200	A	4.5	190	0	0	0	0	170	190	360	59	O	79	X	66.9	O	199	O
Comparative Example 4	3200	A	4.5	220	0	0	0	0	0	220	220	62	O	69	O	58.5	X	200	O
Example 11	3200	A	4.5	200	0	0	0	0	0	200	200	60	O	60	O	65.6	O	198	O
Example 12	3200	A	4.5	0	200	0	0	0	0	200	200	61	O	65	O	66.3	O	197	O
Example 13	3200	A	4.5	0	0	200	0	0	0	200	200	60	O	63	O	66.1	O	197	O
Example 14	3200	A	4.5	0	0	0	200	0	0	200	200	61	O	65	O	67.1	O	201	O
Example 15	3200	A	4.5	0	0	0	0	200	0	200	200	59	O	63	O	66.5	O	199	O

[0059]

[Table 3]

	Blaine value	Clinker type	Limestone	Auxiliary agent mg/kg						Total of amine	Total of auxiliary agent	Pulverization effect		Floodability index		Mortar strength		0 stroke flow	
	cm ² /g			Amine					DEG							28 days			
				%	DEIPA	TIPA	EDIPA	MDEA								BDEA	mg/kg		
Example 16	3200	A	4.5	50	50	0	0	0	120	100	220	60	0	62	0	64.9	0	198	0
Example 17	3200	A	4.5	0	0	0	30	20	20	50	70	71	X	58	0	66.3	0	196	0
Example 18	3200	A	4.5	0	0	80	0	50	100	130	230	60	0	62	0	67.0	0	200	0
Example 19	3200	A	4.5	0	50	0	0	50	120	100	220	60	0	65	0	64.5	0	201	0
Comparative Example 5	3200	A	1.0	50	0	0	0	0	150	50	200	60	0	61	0	59.2	X	163	X
Example 20	3200	A	3.2	50	0	0	0	0	150	50	200	60	0	63	0	65.8	0	198	0
Example 21	3200	A	6.5	50	0	0	0	0	150	50	200	60	0	60	0	65.8	0	198	0
Example 22	3200	A	9.5	50	0	0	0	0	150	50	200	60	0	65	0	63.2	0	198	0
Comparative Example 6	3200	A	11.0	50	0	0	0	0	150	50	200	60	0	66	0	57.6	X	225	0
Comparative Example 7	2700	A	4.5	50	0	0	0	0	150	50	200	60	0	60	0	58.2	X	230	0
Example 23	2850	A	4.5	50	0	0	0	0	150	50	200	60	0	60	0	62.3	0	225	0
Example 24	3450	A	4.5	50	0	0	0	0	150	50	200	60	0	60	0	65.5	0	175	0
Comparative Example 8	3550	A	4.5	50	0	0	0	0	150	50	200	60	0	60	0	63.6	0	154	X
Comparative Example 9	3200	G	4.5	50	0	0	0	0	150	50	200	60	0	60	0	59.5	X	188	0
Comparative Example 10	3200	B	4.5	50	0	0	0	0	150	50	200	60	0	60	0	67.8	0	155	X
Comparative Example 11	3200	C	4.5	50	0	0	0	0	150	50	200	60	0	60	0	58.4	X	180	0
Example 25	3200	D	4.5	50	0	0	0	0	150	50	200	60	0	60	0	65.0	0	181	0
Example 26	3200	E	4.5	50	0	0	0	0	150	50	200	60	0	60	0	66.1	0	178	0
Comparative Example 12	3200	F	4.5	50	0	0	0	0	150	50	200	60	0	60	0	58.4	X	202	0

CLAIMS

[Claim 1] A cement composition comprising:

an ordinary Portland cement clinker comprising 51% to 62%
5 by mass of C_3S and 7% to 10% by mass of C_4AF , which are calculated
by Bogue's formula;

a gypsum;

a limestone; and

an auxiliary agent comprising alkanolamine,

10 wherein a content of the alkanolamine in a total amount
of the ordinary Portland cement clinker, the gypsum, and the
auxiliary agent is 10 to 210 mg/kg,

a content of the limestone in a total amount of the ordinary
Portland cement clinker, the gypsum, the auxiliary agent, and
15 the limestone is 3% to 10% by mass,

a unit cell volume of C_4AF is more than 0.4290 nm^3 , and
Blaine specific surface area is 2,800 to 3,500 cm^2/g .

[Claim 2] The cement composition according to claim 1,

20 wherein a content of the auxiliary agent in the total amount
of the ordinary Portland cement clinker, the gypsum, and the
auxiliary agent is 80 to 350 mg/kg.

[Claim 3] The cement composition according to claim 1 or

25 2, wherein the auxiliary agent comprises an aliphatic polyhydric

alcohol.

[Claim 4] The cement composition according to any one of claims 1 to 3, wherein a content of the gypsum in the total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 0.7% to 2.8% by mass in terms of SO_3 .

[Claim 5] The cement composition according to any one of claims 1 to 4, wherein the alkanolamine is at least one selected from the group consisting of diethanolisopropanolamine, triisopropanolamine, ethanoldiisopropanolamine, N-methyldiethanolamine, and Nn-butyldiethanolamine.

[Claim 6] The cement composition according to claim 3, wherein the aliphatic polyhydric alcohol is at least one selected from the group consisting of glycerin and diethylene glycol.

[Claim 7] A method for producing a cement composition comprising:

producing the cement composition according to any one of claims 1 to 6 by mixing an ordinary Portland cement clinker that comprises 51% to 62% by mass of C_3S and 7% to 10% by mass of C_4AF , which are calculated by Bogue's formula, and that has a unit cell volume of C_4AF of more than 0.4290 nm^3 , a gypsum, a limestone, and an auxiliary agent comprising alkanolamine such that a

blending amount of the alkanolamine in a total amount of the ordinary Portland cement clinker, the gypsum, and the auxiliary agent is 10 to 210 mg/kg and a blending amount of the limestone in a total amount of the ordinary Portland cement clinker, the
5 gypsum, the auxiliary agent, and the limestone is 3% to 10% by mass.