

DESCRIPTION

TITLE OF INVENTION

CEMENT CLINKER AND CEMENT COMPOSITION

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Technical Field

[0001]

The present invention relates to a cement clinker and a cement composition, especially ordinary Portland cement.

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Background Art

[0002]

As a method for improving strength development of mortar, a method for increasing fineness (Blaine's specific surface area) of a cement composition and a method for increasing a content of $3\text{CaO} \cdot \text{SiO}_2$ in a cement composition are known (Non Patent Literature No. 1).

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In addition, TiO_2 and MgO , which are trace components in a cement clinker, give to a mineral composition and a physical property of cement. For example, it has been reported that when a MgO content increases, reactivity of alite decreases and strength development decreases (Non Patent Literature No. 2).

25 Citation List

[0003]

Non Patent Literature

[Non Patent Literature No. 1] Cement Association,
"Common Knowledge of Cement", "4. Types and Applications of
5 Cement", 2004, pp. 11-17

[Non Patent Literature No. 2] Keiji Chabayashi et
al., "Effects of TiO_2 and MgO on clinker mineral composition
and physical properties of cement", Cement and Concrete
Proceedings, vol. 66 (2012), pp. 211-216

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Summary of Invention

Technical Problem

[0004]

However, when the strength development of mortar is
15 increased by means for changing the fineness or mineral
composition of the cement composition, such as increasing
the fineness as in Non Patent Literature No. 1 and
increasing the content of $3\text{CaO}\cdot\text{SiO}_2$, a problem that setting
time is shortened and fluidity is lowered arises.

20 In addition, in order to increase the fineness, a
problem that energy required for pulverizing a cement
clinker increases arises, and when a content of $3\text{CaO}\cdot\text{SiO}_2$ is
to be increased, a problem that a limestone basic unit is
required to be increased arises.

25 All of these are not preferable because the problems

lead to an increase in carbon dioxide emissions and an increase in energy for clinker calcining, which increases an environmental burden.

[0005]

5 Further, as in Non Patent Literature No. 2, it is not possible to obtain a sufficient improvement in the strength development of the mortar only by examining contents of TiO_2 and MgO .

10 Therefore, an object of the present invention is to provide a cement clinker composition capable of improving the strength development of mortar while suppressing an increase in environmental burden by examining a content of each compound in a cement clinker.

15 Solution to Problem

[0006]

20 In cement clinker manufacture and cement manufacture, a physical property of cement is affected by not only main components such as Al_2O_3 but also various trace components, manufacture conditions, or the like.

25 Non Patent Literature No. 2 reports on an influence of TiO_2 and MgO on a clinker mineral composition and a physical property of cement, but simply adjusting the content of these components is not sufficient to improve the strength development of the mortar.

[0007]

Therefore, as a result of detailed examination of components in a cement composition, the present inventors have found that when examining a content of each compound
 5 in $3\text{CaO} \cdot \text{SiO}_2$ (abbreviation: C_3S) and $2\text{CaO} \cdot \text{SiO}_2$ (abbreviation: C_2S), a cement clinker composition capable of improving strength development of mortar while suppressing an increase in environmental burden can be obtained.

That is, the present invention provides the following
 10 [1] to [3].

[1] A cement clinker including:

$3\text{CaO} \cdot \text{SiO}_2$ in a proportion, calculated by Bogue formula, of 50.0% by mass or more and 75.0% by mass or less;

15 $2\text{CaO} \cdot \text{SiO}_2$ in a proportion, calculated by Bogue formula, of 5.0% by mass or more and 25.0% by mass or less;

MgO ;

Na_2O ; and

MnO ,

20 wherein Formula (1) is satisfied.

$$\text{MgO_C}_3\text{S} \times (-0.6) + \text{Na}_2\text{O_C}_3\text{S} \times (15.3) + \text{MgO_C}_2\text{S} \times (-6.9) + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) + \text{MnO_C}_2\text{S} \times (145.7) \geq 5.700 \cdots (1)$$

In the formula,

$\text{MgO_C}_3\text{S}$ represents a content (% by mass) of MgO in $3\text{CaO} \cdot \text{SiO}_2$,

Na₂O_C₃S represents a content (% by mass) of Na₂O in
3CaO·SiO₂,

MgO_C₂S represents the content (% by mass) of MgO in
2CaO·SiO₂,

5 Na₂O_C₂S represents the content (% by mass) of Na₂O in
2CaO·SiO₂, and

MnO_C₂S represents the content (% by mass) of MnO in
2CaO·SiO₂.

[2] The cement clinker according to [1], in which
10 Formula (2) is further satisfied.

$$\text{MgO_C}_2\text{S} \times (-6.9) + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) \\ + \text{MnO_C}_2\text{S} \times (145.7) \geq 4.600 \cdots (2)$$

[3] A cement composition including:

the cement clinker according to [1] or [2]; and
gypsum.

15

Advantageous Effects of Invention

[0008]

According to the present invention, it is possible to
obtain a cement clinker and a cement composition capable of
20 improving strength development of mortar while suppressing
an increase in environmental burden.

Description of Embodiments

[0009]

Hereinafter, a cement clinker and a cement composition of the present invention will be described in detail.

[0010]

[Cement clinker]

5 The cement clinker of the present invention is preferably used for ordinary Portland cement.

[0011]

The cement clinker of the present invention is a main component forming a cement composition, and is manufactured
10 by blending limestone (CaO component), clay (Al₂O₃ component and SiO₂ component), silica stone (SiO₂ component), an iron oxide raw material (Fe₂O₃ component), and the like and firing. The cement clinker of the present invention may contain industrial waste or the like such as coal ash,
15 construction-generated soil, steelmaking slag, blast furnace slag, converter slag, by-product gypsum, municipal waste incineration ash, and a by-product produced during a production process, as raw materials.

Contents of SiO₂, Al₂O₃, Fe₂O₃ and CaO are measured
20 according to JIS R 5204:2019 "Analysis method for cement by X-ray fluorescence".

[0012]

<Main components>

The content of the SiO₂ of the cement clinker of the
25 present invention is preferably 15.00% by mass or more,

more preferably 17.00% by mass or more, and still more preferably 18.00% by mass or more, and is preferably 30.00% by mass or less, more preferably 25.00% by mass or less, and still more preferably 23.00% by mass or less.

5 [0013]

The content ($W_{Al_2O_3}$ % by mass) of the Al_2O_3 of the cement clinker of the present invention is preferably 2.00% by mass or more, more preferably 4.00% by mass or more, and still more preferably 4.50% by mass or more, and is
10 preferably 10.00% by mass or less, more preferably 8.00% by mass or less, and still more preferably 7.00% by mass or less.

[0014]

15 The content ($W_{Fe_2O_3}$ % by mass) of the Fe_2O_3 of the cement clinker of the present invention is preferably 1.00% by mass or more, more preferably 1.50% by mass or more, and still more preferably 2.00% by mass or more, and is preferably 10.00% by mass or less, more preferably 7.00% by
20 mass or less, and still more preferably 5.00% by mass or less.

[0015]

The content of the CaO of the cement clinker of the present invention is preferably 50.00% by mass or more,
25 more preferably 55.00% by mass or more, and still more

preferably 60.00% by mass or more, and is preferably 80.00% by mass or less, more preferably 75.00% by mass or less, and still more preferably 70.00% by mass or less.

[0016]

5 <Trace components>

The cement clinker of the present invention contains MgO, Na₂O, and MnO, as trace components. Each content of the MgO, the Na₂O, and the MnO is measured in accordance with JIS R 5204:2019 "Analysis method for cement by X-ray
10 fluorescence".

The MgO is introduced into the cement clinker, for example, by using a slag containing a large amount of MgO as a raw material for the cement clinker.

The Na₂O is introduced into the cement clinker, for
15 example, by using construction-generated soil as a raw material for the cement clinker.

The MnO is introduced into the cement clinker by using, for example, a blast furnace slag and a converter slag as raw materials for the cement clinker.

20 [0017]

The content (W_{MgO} % by mass) of the MgO of the cement clinker of the present invention is preferably 0.05% by mass or more, more preferably 0.2% by mass or more, and still more preferably 0.5% by mass or more, and is
25 preferably 5.00% by mass or less, more preferably 3.00% by

mass or less, and still more preferably 2.5% by mass or less.

[0018]

The content (W_{Na_2O} % by mass) of the Na_2O of the cement
 5 clinker of the present invention is preferably 0.10% by mass or more and more preferably 0.15% by mass or more, and is preferably 1.00% by mass or less, more preferably 0.80% by mass or less, and still more preferably 0.50% by mass or less.

10 [0019]

The MnO content (W_{MnO} % by mass) of the cement clinker of the present invention is preferably 0.01% by mass or more and more preferably 0.02% by mass or more, and preferably 0.50% by mass or less, more preferably 0.30% by
 15 mass or less, and still more preferably 0.20% by mass or less.

[0020]

<Formula (1)>

In $3CaO \cdot SiO_2$ (abbreviation: C_3S) and $2CaO \cdot SiO_2$
 20 (abbreviation: C_2S) in the cement clinker of the present invention, MgO_{C_3S} (content (% by mass) of MgO in $3CaO \cdot SiO_2$), $Na_2O_{C_3S}$ (content (% by mass) of Na_2O in $3CaO \cdot SiO_2$), MgO_{C_2S} (content (% by mass) of MgO in $2CaO \cdot SiO_2$), $Na_2O_{C_2S}$ (content (% by mass) of Na_2O in
 25 $2CaO \cdot SiO_2$), MnO_{C_2S} (content (% by mass) of MnO in

2CaO·SiO₂) satisfy the relationship of Formula (1).

These contents are determined by an EPMA measurement to be described later.

[0021]

$$\begin{aligned} & \text{MgO_C}_3\text{S} \times (-0.6) + \text{Na}_2\text{O_C}_3\text{S} \times (15.3) + \text{MgO_C}_2\text{S} \times (-6.9) \\ 5 \quad & + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) + \text{MnO_C}_2\text{S} \times (145.7) \geq 5.700 \cdots (1) \end{aligned}$$

[0022]

Non Patent Literature No. 2 examines the mineral composition of C₃S and C₂S based on a composition of the TiO₂ and the MgO in the cement clinker as described above.

10 However in the present invention, by examining a chemical composition in C₃S and C₂S, the strength development of the mortar manufactured from the cement clinker is improved.

The chemical composition of the C₃S and the C₂S can be appropriately adjusted depending on raw materials to be
15 used and combinations thereof.

[0023]

A left side of Formula (1) is 5.700 or more, and from a viewpoint of the strength development of the mortar, preferably 5.900 or more, more preferably 6.000 or more,
20 and still more preferably 6.100 or more.

An upper limit of the left side of Formula (1) is not particularly limited, and from the viewpoint of ease of procurement and manufacture of raw materials, is more preferably 12.000 or less, still more preferably 11.000 or

less, and still more preferably 10.000 or less.

[0024]

<MgO_C₃S, Na₂O_C₃S, MgO_C₂S, Na₂O_C₂S and MnO_C₂S>

The MgO_C₃S is adjusted together with other components
5 according to the value on the left side of Formula (1), and
is preferably 0.100 or more, more preferably 0.300 or more,
and still more preferably 0.400 or more and more preferably
2.000 or less, still more preferably 1.500 or less, and
still further preferably 1.000 or less.

10 [0025]

The Na₂O_C₃S is adjusted together with other
components according to the value on the left side of
Formula (1), and is preferably 0.050 or more, more
preferably 0.070 or more, and still more preferably 0.080
15 or more and more preferably 1.000 or less, still more
preferably 0.500 or less, and still further preferably
0.300 or less.

The MgO_C₂S is adjusted together with other components
according to the value on the left side of Formula (1), and
20 is preferably 0.010 or more, more preferably 0.100 or more,
and still more preferably 0.200 or more and more preferably
2.000 or less, still more preferably 1.000 or less, and
still further preferably 0.700 or less.

[0026]

25 The Na₂O_C₂S is adjusted together with other

components according to the value on the left side of Formula (1), and is preferably 0.050 or more, more preferably 0.100 or more, and still more preferably 0.200 or more and more preferably 2.000 or less, still more preferably 1.200 or less, and still further preferably 0.800 or less.

The $\text{MnO} \cdot \text{C}_2\text{S}$ is adjusted together with other components according to the value on the left side of Formula (1), and is preferably 0.001 or more, more preferably 0.010 or more, and still more preferably 0.020 or more and more preferably 0.200 or less, still more preferably 0.100 or less, and still further preferably 0.070 or less.

[0027]

<Cement clinker composition>

The cement clinker of the present invention contains $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (abbreviation: C_3A) and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (abbreviations: C_4AF), in addition to the $3\text{CaO} \cdot \text{SiO}_2$ (abbreviation: C_3S) and the $2\text{CaO} \cdot \text{SiO}_2$ (abbreviation: C_2S). The cement clinker is formed of main minerals of alite (C_3S) and belite (C_2S) and an interstitial phase or the like of an aluminate phase (C_3A) and a ferrite phase (C_4AF) existing between crystals of the main minerals.

[0028]

Proportions of C_3S , C_2S , C_3A , and C_4AF in the cement clinker are determined from proportions of CaO , SiO_2 , Al_2O_3 ,

and Fe_2O_3 , measured by JIS R 5204:2019 "Analysis method for cement by X-ray fluorescence" in cement clinker, by a calculation called Bogue formula in a field of cement chemistry (for example, see "Science of Cement", translated
5 by Masaki Daimon, Uchida Old Tsuruno (1989), p. 11).

[0029]

<Proportion of $3\text{CaO}\cdot\text{SiO}_2$ (C_3S)>

The proportion of the $3\text{CaO}\cdot\text{SiO}_2$ calculated by the Bogue formula in the cement clinker of the present
10 invention is preferably 50.0% by mass or more, more preferably 52.0% by mass or more, still more preferably 54.0% by mass or more because the strength development of the concrete and the mortar manufactured by using the cement clinker can be set to a practical level, and is more
15 preferably 75.0% by mass or less, more preferably 70.0% by mass or less, and still more preferably 65.0% by mass or less because the heat of hydration of the cement composition can be suppressed.

[0030]

20 <Proportion of $2\text{CaO}\cdot\text{SiO}_2$ (C_2S)>

The proportion of the $2\text{CaO}\cdot\text{SiO}_2$ calculated by the Bogue formula in the cement clinker of the present invention is preferably 5.0% by mass or more, more preferably 10.0% by mass or more, and still more preferably
25 15.0% by mass or more because it is suppressed that

3CaO·SiO₂ increases and the heat of hydration of the cement composition becomes too high, and is preferably 25.0% by mass or less, and more preferably 24.0% by mass or less because the short-term strength of concrete and mortar manufactured by the cement clinker can be raised to a practical level or higher.

[0031]

<Total proportion of 3CaO·Al₂O₃ (C₃A) and 4CaO·Al₂O₃·Fe₂O₃ (C₄AF)>

10 A total proportion of 3CaO·Al₂O₃ and 4CaO·Al₂O₃·Fe₂O₃ calculated by the Bogue formula in the cement clinker of the present invention is preferably 15.0% by mass or more, more preferably 16.0% by mass or more, and still more preferably 17.0% by mass or more, because when the amount
15 of a liquid phase generated during the calcining of the cement clinker composition is small, the solid-phase-liquid phase reaction due to the intervention of the liquid phase does not proceed rapidly, and the calcining of the cement clinker composition may be insufficient, and the calcining
20 of the cement clinker composition may be insufficient, and also dust is scattered during the cement kiln and the radiant heat from a burner is blocked, so calcining of the cement clinker may not be performed efficiently, and is preferably 22.0% by mass or less and more preferably 21.0%
25 by mass or less, because the short-term strength of

concrete and mortar produced using the cement clinker can be set to a practical level or higher.

[0032]

<Proportion of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A)>

5 The proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ calculated by the Bogue formula in the cement clinker of the present invention is preferably 3.0% by mass or more, more preferably 5.0% by mass or more, and still more preferably 7.0% by mass or more, because the decrease in viscosity of
10 the liquid phase generated during calcining of cement clinker is suppressed, the granulation of cement clinker is appropriately proceeded, it is suppressed that a layer pressure in the clinker cooler becomes unstable due to decrease in the particle size of cement clinker and the
15 heat of hydration can be reduced, and is preferably 15.0% by mass or less and more preferably 12.0% by mass or less, because the layer pressure in the clinker cooler becomes constant, and the cement clinker can be quenched.

[0033]

20 <Proportion of $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (C_4AF)>

 The proportion of the $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ calculated by the Bogue formula in the cement clinker of the present invention is preferably 5.0% by mass or more, more preferably 7.0% by mass or more, and still more preferably
25 8.3% by mass or more because the heat of hydration of the

cement composition can be suppressed, and is preferably 13.0% by mass or less and more preferably 11.0% by mass or less because the short-term strength of concrete and mortar manufactured by the cement clinker can be raised to a practical level or higher.

[0034]

<Formula (2)>

It is also preferable that $\text{MgO_C}_2\text{S}$, $\text{Na}_2\text{O_C}_2\text{S}$ and $\text{MnO_C}_2\text{S}$ in C_2S of the cement clinker of the present invention satisfy the relationship of Formula (2).

[0035]

$$\text{MgO_C}_2\text{S} \times (-6.9) + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) + \text{MnO_C}_2\text{S} \times (145.7) \geq 4.600 \cdots (2)$$

[0036]

A left side of Formula (2) is, from a viewpoint of the strength development of the mortar, preferably 4.600 or more, more preferably 4.700 or more, and still more preferably 4.800 or more.

An upper limit of the left side of Formula (2) is not particularly limited, and from the viewpoint of ease of procurement and manufacture of raw materials, is more preferably 10.000 or less, still more preferably 9.000 or less, and still further preferably 8.500 or less.

[0037]

[Method for manufacturing cement clinker]

A clinker of the present invention can be manufactured, for example, as follows.

As a clinker raw material, those containing at least Mg, Na, and Mn, in addition to Ca, Si, Al, and Fe are used.

5 As long as the raw material contains the above elements, any form thereof such as an elemental substance, an oxide, a carbon oxide can be used and mixtures thereof can be used. Examples of natural raw materials include limestone, clay, silica stone, and iron oxide raw materials. Examples
10 of industrial raw materials include waste raw materials containing the above elements, a blast furnace slag, fly ash, and the like. Regarding the mixing proportion of the clinker raw material, it is preferable to mix the raw material so as to have a component composition
15 corresponding to the target Bogue formula value and satisfy Formula (1).

[0038]

Then, the clinker raw material mixed in a composition so as to obtain the targeted clinker is calcinated under a
20 normal calcining condition and cooled. Firing is usually performed using an electric furnace, a rotary kiln, or the like. Examples of a calcining method include a method including: a first calcining step in which a clinker raw material is heated and calcinated at a predetermined first
25 calcining temperature for a first calcining time; a

temperature raising step of raising a temperature, after
the first calcining step, from the first calcining
temperature to a predetermined second calcining temperature
over a predetermined temperature raising time; and a second
5 calcining step of heating and calcining, after the
temperature raising step, at the second calcining
temperature for a predetermined second calcining time.

The temperature and time of each step may be the
conditions usually carried out, and the cement clinker can
10 be manufactured by quenching the calcined product.

[0039]

[Cement composition]

The cement composition of the present invention
contains the cement clinker and gypsum. The Blaine's
15 specific surface area of the cement used in the present
invention is preferably 3000 cm²/g or more and 3400 cm²/g or
less, and more preferably 3100 cm²/g or more and 3300 cm²/g
or less.

[Gypsum]

20 A proportion of the gypsum in the cement composition
of the present invention is preferably 0.5% to 2.5% by
mass, and more preferably 1.0% to 1.8% by mass in terms of
SO₃ equivalent. When setting the proportion of the gypsum
to the range, drying shrinkage of the cement composition
25 can be made appropriate, and strength exhibited by the

cement composition can be increased. A proportion of SO_3 in the gypsum can be measured in accordance with JIS R 5202:2010 "Chemical analysis method for Portland cement". A proportion of the mass of the gypsum converted to SO_3 in the cement composition can be determined from a blending amount of the gypsum and the proportion of the SO_3 contained in the gypsum.

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

10 [0040]

<Other components>

Fly ash, blast furnace slag, silica fume, or the like can be further added to the cement composition of the present invention in order to control fluidity, a hydration rate, or strength development. Further, an AE water reducing agent, a high-performance water reducing agent, or a high-performance AE water reducing agent, particularly a polycarboxylate-based high-performance AE water reducing agent, can be added to the cement composition of the present invention.

15

20

[0041]

[Mortar and concrete]

Cement milk can be prepared by mixing the cement composition of the present invention with water, mortar can be prepared by mixing with water and sand, and concrete can

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be manufactured by mixing sand and gravel. Further, when producing the mortar or the concrete from the cement composition, a blast furnace slag, fly ash, or the like can be added.

5 Examples

[0042]

Hereinafter, the present invention will be described in more detail with reference to examples. However, the present invention is not limited to the following examples.

10 1. Measurement and evaluation

1-1. Clinker composition

A chemical composition (content rate of each component) in cement clinkers of Examples and Comparative Examples was measured in accordance with JIS R 5204:2019
15 "Analysis method for cement by X-ray fluorescence". Results are shown in Table 1.

A mineral composition was calculated from the obtained mass proportions of CaO, SiO₂, Al₂O₃, and Fe₂O₃ by using the following Bogue formula. Results are shown in Table 2.

20
$$C_3S = (4.07 \times CaO) - (7.60 \times SiO_2) - (6.72 \times Al_2O_3) - (1.43 \times Fe_2O_3)$$

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

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

$$C_4AF = 3.04 \times Fe_2O_3$$

25 Further, the value on the left side of Formula (1) was

calculated using the obtained content rate of each component. Results are shown in Table 3.

[0043]

1-2. EPMA measurement

5 The cement clinker of Examples and Comparative Examples was pulverized to a particle size of about 1 to 2 mm to adjust the particle size. The obtained particles were embedded in an epoxy resin, and then the resin surface was mirror-polished. After the mirror polishing, carbon vapor
10 deposition was performed on the resin surface to produce a sample for EPMA measurement.

 An EPMAJXA-8200 manufactured by JEOL Ltd. was used as a measuring device, and a structure image of the cement clinker particles on the mirror surface of the sample was
15 observed under the following conditions. In the structure image, each mineral was specified based on the characteristics of above (a) to (d).

 Each mineral was identified based on characteristics of (a) to (d).

20 (a) C_3S : Polygonal particle, light gray, and tens of μm

 (b) C_2S : Elliptical particle, dark gray, and tens of μm

 (c) C_3A : Amorphous structure observed between silicate
25 phases, dark gray, and several μm to a dozen μm

(d) C_4AF : Amorphous structure observed between silicate phases, white, and several μm to a dozen μm

A characteristic X-ray was analyzed at 20 points for each of the four minerals, with acceleration voltage: 15
 5 kV, irradiation electric current: 3.0×10^{-8} A, beam diameter: about 1 μm , and a correction calculation method: oxide-ZAF method.

Among these, for C_3S , the analysis points within the range of $2.7 < CaO \text{ content rate } (\%)/SiO_2 \text{ content rate } (\%) <$
 10 3.3 were adopted, and the average value obtained was adopted as the chemical composition (% by mass) in C_3S .

Among these, for C_2S , the analysis points within the range of $1.8 < CaO \text{ content rate } (\%)/SiO_2 \text{ content rate } (\%) <$
 15 2.5 were adopted, and the average value obtained was adopted as the chemical composition (% by mass) in C_2S .

[0044]

1-3. Mortar strength at 28 days of age (strength development, 28d strength)

For the mortar strength at 28 days of age using the
 20 cement clinker of Examples and Comparative Examples, according to JIS R 5201 "Physical test method for cement:
 10. 4 Method for producing specimens", mortar prepared from cement compositions was placed in three metal molds of 40 x
 40 x 160 mm, respectively, and 24 hours later, the mold was
 25 removed to prepare three mortar specimens. The material was

cured in water at 20°C until 28 days of age, and the compressive strength was measured according to JIS R 5201 "Physical test method for cement: 10.5 measurement".

[0045]

5 1-4. Setting measurement method

The cement paste was prepared according to JIS R 5201:2015 "Physical testing methods for cement", the standard soft water amount was determined, and then the start time and end time were measured with the standard
10 soft paste.

[0046]

2. Preparation of cement composition

2-1. Clinker

As raw materials for the cement clinker, calcium
15 carbonate (manufactured by Kishida Chemical Co., Ltd., reagent first grade, CaCO_3), silicon dioxide (manufactured by Kanto Chemical Co., Ltd., reagent first grade, SiO_2), aluminum oxide (manufactured by Kanto Chemical Co., Ltd., reagent first grade, Al_2O_3), iron oxide (III) (manufactured
20 by Kanto Chemical Co., Ltd., reagent special grade, Fe_2O_3), basic magnesium carbonate (manufactured by Kishida Chemical Co., Ltd., reagent special grade, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), sodium carbonate (manufactured by Kishida Chemical Co., Ltd., special grade, Na_2CO_3), potassium carbonate
25 (manufactured by Kanto Chemical Co., Ltd., reagent first

grade, K_2CO_3), calcium sulfate dihydrate (manufactured by Kishida Chemical Co., Ltd., reagent first grade, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), titanium dioxide (manufactured by Kanto Chemical Co., Ltd., reagent special grade, TiO_2), tricalcium phosphate (manufactured by Kishida Chemical Co., Ltd., reagent first grade, $\text{Ca}_3(\text{PO}_4)_2$), manganese oxide (manufactured by Kanto Chemical Co., Ltd., Cica first grade, MnO_2), and zinc oxide (manufactured by Kanto Chemical Co., Ltd., reagent special grade, ZnO) were used.

10 [0047]

The raw materials blended with varying the blending amount were put into an electric furnace and calcined at 1000°C for 30 minutes. Then, a temperature was raised from 1000°C to 1450°C over 45 minutes, and further calcined at
15 1450°C for 30 minutes.

Then, the calcined product was quenched by taking the calcined product into an atmosphere to prepare cement clinkers of Examples 1 to 6 and Comparative Example 1.

[0048]

20 2-2. Preparation of cement composition

Semi-hydrated gypsum (manufactured by Kanto Chemical Co., Inc., semi-hydrated gypsum, model number: 07108-01 (calcined gypsum deer first grade) with SO_3 equivalent amount of 1.5% by mass) was blended with the prepared
25 cement clinker. The compound was pulverized with a ball

mill so that the Blaine's specific surface area value became in a range of about $3200 \pm 200 \text{ cm}^2/\text{g}$ to prepare cement compositions of Examples 1 to 5 and Comparative Examples 1 and 3.

5 [0049]

2-3. Preparation of mortar

Mortar was adjusted from the cement compositions of Examples and Comparative Examples in accordance with JIS R 5201:2015 "Physical testing methods for cement". The
10 obtained mortar was cast into three metal molds having a size of 40 mm × 40 mm × 160 mm, and after 24 hours, the mortar was demolded to prepare three specimens.

[0050]

[Table 1]

Table 1	Chemical composition (% by mass)										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO
Example 1	21.90	5.58	2.82	65.84	1.66	0.45	0.36	0.46	0.32	0.35	0.05
Example 2	21.64	6.16	3.20	65.46	1.36	0.71	0.33	0.29	0.33	0.26	0.06
Example 3	22.31	5.26	3.55	65.88	0.99	0.60	0.31	0.45	0.27	0.11	0.06
Example 4	22.30	5.72	3.14	65.99	1.03	0.47	0.26	0.40	0.29	0.15	0.05
Example 5	22.05	5.63	3.31	65.71	0.99	0.29	0.38	0.36	0.34	0.65	0.09
Comparative Example 1	21.77	5.51	3.18	65.29	2.53	0.34	0.24	0.37	0.29	0.24	0.05
Comparative Example 2	21.65	5.59	3.43	65.83	1.44	0.53	0.27	0.45	0.32	0.25	0.05
Comparative Example 3	22.57	5.27	3.56	65.54	1.20	0.49	0.31	0.42	0.27	0.12	0.06

[0051]

[Table 2]

Table 2	Mineral composition (% by mass)					MgO_C ₃ S (% by mass)	Na ₂ O_C ₃ S (% by mass)	MgO_C ₂ S (% by mass)	Na ₂ O_C ₂ S (% by mass)	MnO_C ₂ S (% by mass)
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₃ A +C ₄ AF					
Example 1	60.0	17.6	10.0	8.6	18.6	0.903	0.116	0.437	0.487	0.037
Example 2	56.0	19.9	10.9	9.7	20.6	0.851	0.097	0.469	0.413	0.045
Example 3	58.2	20.2	7.9	10.8	18.7	0.637	0.139	0.391	0.537	0.034
Example 4	56.2	21.6	9.9	9.5	19.4	0.575	0.095	0.276	0.383	0.055
Example 5	57.3	20.1	9.3	10.1	19.4	0.639	0.141	0.315	0.683	0.044
Comparative Example 1	58.7	18.2	9.2	9.7	18.9	1.438	0.128	0.652	0.442	0.030
Comparative Example 2	60.9	16.2	9.0	10.4	19.4	0.869	0.093	0.511	0.373	0.039
Comparative Example 3	54.7	23.5	7.9	10.8	18.8	0.725	0.100	0.452	0.359	0.039

[0052]

[Table 3]

Table 3	Left side of Formula (1)	Left side of Formula (2)	28d strength (N/mm ²)	Water amount (% by mass)	Setting start time (minutes)	Setting end time (minutes)
Example 1	6.141	4.908	60.5	29.4	165	235
Example 2	6.442	5.468	64.1	28.0	130	215
Example 3	6.793	5.048	63.9	27.6	110	195
Example 4	9.209	8.101	63.9	27.8	115	220
Example 5	9.563	7.789	67.5	27.4	160	265
Comparative Example 1	3.266	2.171	59.2	27.7	130	210
Comparative Example 2	4.998	4.096	59.3	27.7	140	240
Comparative Example 3	5.525	4.430	57.0	27.0	155	260

[0053]

In Examples 1 to 5 and Comparative Examples 1 to 3,
the TiO_2 focused on in Non Patent Literature No. 2 is set to
about 0.30% by mass, and evaluation results of the cement
5 clinker with the value on the left side of Formula (1) and
mortar using the same were obtained.

It was found that all of Examples 1 to 5 were superior
in 28d strength compared to Comparative Examples 1 to 3.

Further, in the invention described in Non Patent
10 Literature No. 1, the setting time was shortened by
changing the fineness and the mineral composition, but it
was confirmed that the setting time was not shortened in
the present invention as shown in Table 3.

[0054]

15 Example 2 is a cement clinker adjusted to satisfy
Formula (1) by decreasing $\text{MgO_C}_2\text{S}$ and $\text{Na}_2\text{O_C}_2\text{S}$ and
increasing $\text{MnO_C}_2\text{S}$ from Example 1. Example 4 is a cement
clinker adjusted to satisfy Formula (1) by decreasing
 $\text{Na}_2\text{O_C}_3\text{S}$ and $\text{Na}_2\text{O_C}_2\text{S}$ and increasing $\text{MnO_C}_2\text{S}$. In both cases,
20 the 28d strength became a large value.

In Example 3, $\text{MnO_C}_2\text{S}$ was reduced from Example 1, but
the 28d strength became a large value by adjusting so as to
satisfy Formula (1).

[0055]

25 As described above, it was found that when adjusting

the $\text{MgO_C}_3\text{S}$, the $\text{Na}_2\text{O_C}_3\text{S}$, the $\text{MgO_C}_2\text{S}$, the $\text{Na}_2\text{O_C}_2\text{S}$, and the $\text{MnO_C}_2\text{S}$ so as to satisfy Formula (1), a cement clinker with excellent properties can be obtained.

CLAIMS

1. A cement clinker comprising:

$3\text{CaO}\cdot\text{SiO}_2$ in a proportion, calculated by Bogue

5 formula, of 50.0% by mass or more and 75.0% by mass or less;

$2\text{CaO}\cdot\text{SiO}_2$ in a proportion, calculated by Bogue

formula, of 5.0% by mass or more and 25.0% by mass or less;

MgO;

10 Na_2O ; and

MnO,

wherein Formula (1) is satisfied,

$$\text{MgO_C}_3\text{S} \times (-0.6) + \text{Na}_2\text{O_C}_3\text{S} \times (15.3) + \text{MgO_C}_2\text{S} \times (-6.9) \\ + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) + \text{MnO_C}_2\text{S} \times (145.7) \geq 5.700 \cdots (1)$$

in the formula,

15 $\text{MgO_C}_3\text{S}$ represents a content (% by mass) of MgO in $3\text{CaO}\cdot\text{SiO}_2$,

$\text{Na}_2\text{O_C}_3\text{S}$ represents a content (% by mass) of Na_2O in $3\text{CaO}\cdot\text{SiO}_2$,

$\text{MgO_C}_2\text{S}$ represents a content (% by mass) of MgO in
20 $2\text{CaO}\cdot\text{SiO}_2$,

$\text{Na}_2\text{O_C}_2\text{S}$ represents a content (% by mass) of Na_2O in $2\text{CaO}\cdot\text{SiO}_2$, and

$\text{MnO_C}_2\text{S}$ represents a content (% by mass) of MnO in $2\text{CaO}\cdot\text{SiO}_2$.

2. The cement clinker according to claim 1,
wherein Formula (2) is further satisfied

$$\text{MgO_C}_2\text{S} \times (-6.9) + \text{Na}_2\text{O_C}_2\text{S} \times (5.2) \\ + \text{MnO_C}_2\text{S} \times (145.7) \geq 4.600 \cdots (2).$$

5

3. A cement composition comprising:
the cement clinker according to claim 1 or 2; and
gypsum.