

DESCRIPTION

TITLE OF INVENTION

CEMENT CLINKER, CEMENT COMPOSITION, AND CEMENT CLINKER

5

PRODUCTION METHOD

Technical Field

[0001]

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

Background Art

[0002]

From the viewpoint of suppressing cracks in concrete,
15 a cement composition having a low heat of hydration is
required. For example, according to "Common Specifications
for Civil Engineering Work (revised in April 2019)" (Kanto
Regional Development Bureau, Ministry of Land,
Infrastructure, Transport and Tourism), Vol. 2 "Materials",
20 Section 6 "Cement and Admixtures", 2-2-6 -2 "Cement", and
table 2-2-18 "Quality of ordinary Portland cement",
regarding the heat of hydration of cement, control target
values of 350 J/g or less at 7 days of age and 400 J/g or
less at 28 days of age are shown.

25

[0003]

In recent years, various wastes and by-products containing a large amount of Al, such as coal ash and construction-generated soil, have been used as cement raw materials. However, when these wastes and by-products are used, the amount of C₃A in a mineral composition of a cement clinker increases, and the heat of hydration increases. In a case where the wastes and by-products are used as raw materials of the cement clinker, the amount used is currently limited.

10 [0004]

As a method for reducing the heat of hydration of a cement composition, a method for controlling the mineral composition of C₃S and C₃A to a low mineral composition such as moderate heat Portland cement and low heat Portland cement, or a method for mixing with a blast furnace slag is known (for example, Non Patent Literature No. 1 and Non Patent Literature No. 2).

[0005]

Non Patent Literature No. 3 reports an influence of TiO₂ and MgO, which are trace components in a cement clinker, on a mineral composition and physical properties of cement. Non Patent Literature No. 3 discloses that as a MgO content increases, an aluminate phase (C₃A) tends to decrease and heat of hydration tends to decrease, and furthermore, the more the total content of MgO and TiO₂, the

smaller the heat of hydration tends to be.

Citation List

Non Patent Literature

5 [0006]

[Non Patent Literature No. 1] "C & C Encyclopedia-
Basic Explanation of Cement and Concrete Chemistry",
published by Cement Association, July 1996, pp. 17-18

[Non Patent Literature No. 2] "Common Knowledge of
10 Cement", published by Cement Association, January 2007, pp.
13-15

[Non Patent Literature No. 3] Keiji Chabayashi et
al., "Effects of TiO_2 and MgO on clinker mineral composition
and physical properties of cement", Cement and Concrete
15 Proceedings, vol. 66 (2012), pp. 211-216

Summary of Invention

Technical Problem

[0007]

20 As in Non Patent Literature No. 3, it is also possible
to reduce the heat of hydration by the content of MgO and
 TiO_2 in the clinker. However, various trace components are
introduced into the clinker actually produced, which is
derived from industrial waste and by-products. In Non
25 Patent Literature No. 3, no consideration is given to an

influence of other trace components on physical properties such as heat of hydration.

[0008]

The present invention has been made in view of above
5 problems, and an object of the present invention is to
provide a cement clinker capable of reducing heat of
hydration and a cement composition containing the cement
clinker.

10 Solution to Problem

[0009]

In actual cement clinker manufacture and cement
manufacture, a mineral composition and a physical property
of cement are affected by various trace components in
15 addition to MgO and TiO_2 , manufacture conditions, or the
like. As a result of investigating a relationship between
heat of hydration and a clinker having different
manufacture conditions such as a blending amount of a trace
component, the inventors of the present application focused
20 on a chemical component in a mineral composition of the
clinker. As a result, it was found that particularly a
content of a trace component in an aluminate phase (C_3A)
greatly affects the heat of hydration, and the present
invention was completed.

25 [0010]

That is, in order to solve the above problems, the present invention provides the following <1> to <5>.

<1> A cement clinker including: $3\text{CaO}\cdot\text{SiO}_2$ in a proportion, calculated by Bogue formula, of 50% to 75% by mass; $2\text{CaO}\cdot\text{SiO}_2$ in a proportion, calculated by Bogue formula, of 5% to 25% by mass; $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ in a total proportion, calculated by Bogue formula, of 15% to 22% by mass; MgO ; TiO_2 ; MnO ; and ZnO , in which Formula (1) is satisfied.

$$C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$$

In Formula (1),

$C_{\text{Mg-C3A}}$ represents a content rate (% by mass) of MgO in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Ti-C3A}}$ represents a content rate (% by mass) of TiO_2 in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Mn-C3A}}$ represents a content rate (% by mass) of MnO in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and

$C_{\text{Zn-C3A}}$ represents a content rate (% by mass) of ZnO in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

<2> The cement clinker according to <1>, in which a content rate of Fe_2O_3 in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ is less than 6.32% by mass.

<3> The cement clinker according to <1> or <2>, in which the content rate of TiO_2 is less than 0.24% by mass.

<4> A cement composition including: the cement clinker

according to any one of <1> to <3>; and gypsum.

<5> A method for manufacturing a cement clinker,
including: a step of blending raw materials; and a step of
calcining the raw materials blended, in which a cement
5 clinker after calcining contains $3\text{CaO}\cdot\text{SiO}_2$ in a proportion,
calculated by Bogue formula, of 50% to 75% by mass,
 $2\text{CaO}\cdot\text{SiO}_2$ in a proportion, calculated by Bogue formula, of
5% to 25% by mass, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ in a total
proportion, calculated by Bogue formula, of 15% to 22% by
10 mass, MgO, TiO_2 , MnO, and ZnO, and Formula (1) is
satisfied.

$$C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$$

In Formula (1),

$C_{\text{Mg-C3A}}$ represents a content rate (% by mass) of MgO in
15 $3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Ti-C3A}}$ represents a content rate (% by mass) of TiO_2 in
 $3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Mn-C3A}}$ represents a content rate (% by mass) of MnO in
 $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and

20 $C_{\text{Zn-C3A}}$ represents a content rate (% by mass) of ZnO in
 $3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

Advantageous Effects of Invention

[0011]

25 According to the present invention, it is possible to

obtain a cement clinker capable of reducing heat of hydration. When using the cement clinker of the present invention, a cement composition having low heat of hydration can be obtained.

5

Description of Embodiments

[0012]

Hereinafter, a cement clinker and a cement composition of the present invention will be described in detail. The notation of the numerical range of "AA to BB" in the present specification means "AA or more and BB or less".

10

[0013]

[Cement clinker]

The cement clinker of the present invention includes:
 3CaO·SiO₂ in a proportion, calculated by Bogue formula, of 50% to 75% by mass; 2CaO·SiO₂ in a proportion, calculated by Bogue formula, of 5% to 25% by mass; 3CaO·Al₂O₃ and 4CaO·Al₂O₃·Fe₂O₃ in a total proportion, calculated by Bogue formula, of 15% to 22% by mass; MgO; TiO₂; MnO; and ZnO, in which Formula (1) is satisfied.

15

20

$$C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$$

In Formula (1),

$C_{\text{Mg-C3A}}$ represents a content rate (% by mass) of MgO in 3CaO·Al₂O₃,

25

$C_{\text{Ti-C3A}}$ represents a content rate (% by mass) of TiO₂ in

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Mn-C}_3\text{A}}$ represents a content rate (% by mass) of MnO in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and

$C_{\text{Zn-C}_3\text{A}}$ represents a content rate (% by mass) of ZnO in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

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

[0014]

The cement clinker of the present invention is a main composition forming a cement composition, and is manufactured by blending limestone (CaO component), clay (Al_2O_3 component and SiO_2 component), silica stone (SiO_2 component), an iron oxide raw material (Fe_2O_3 component), and the like and calcining. The cement clinker of the present invention may contain industrial waste or the like such as coal ash, construction-generated soil, blast furnace slag, converter slag, by-product gypsum, and municipal waste incineration ash, as raw materials.

The cement clinker of the present invention contains $3\text{CaO}\cdot\text{SiO}_2$ (abbreviation: C_3S), $2\text{CaO}\cdot\text{SiO}_2$ (abbreviation: C_2S), $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (abbreviation: C_3A), and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (abbreviations: C_4AF). 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.

[0015]

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 by Masaki Daimon, Uchida Old Tsuruno (1989), p. 11).

[0016]

10 <Proportion of $3CaO \cdot SiO_2$ (C_3S)>

The proportion of the $3CaO \cdot SiO_2$ calculated by the Bogue formula in the cement clinker of the present invention is 50% to 75% by mass. When the proportion of the $3CaO \cdot SiO_2$ calculated by the Bogue formula is less than 50% by mass, a strength of concrete or mortar expressed by the cement clinker may decrease in some cases. When the proportion of the $3CaO \cdot SiO_2$ calculated by the Bogue formula is larger than 75% by mass, heat of hydration of a cement composition may become too high in some cases. The proportion of the $3CaO \cdot SiO_2$ calculated by the Bogue formula is preferably 50% to 70% by mass, more preferably 55% to 70% by mass, and still more preferably 55% to 67% by mass.

[0017]

<Proportion of $2CaO \cdot SiO_2$ (C_2S)>

25 The proportion of the $2CaO \cdot SiO_2$ calculated by the

Bogue formula in the cement clinker of the present invention is 5% to 25% by mass. When the proportion of the $2\text{CaO}\cdot\text{SiO}_2$ calculated by the Bogue formula is less than 5% by mass, the proportion of the $3\text{CaO}\cdot\text{SiO}_2$ becomes high as a result, and the heat of hydration of a cement composition may become too high in some cases. Also, when the proportion of the $2\text{CaO}\cdot\text{SiO}_2$ calculated by the Bogue formula becomes more than 25% by mass, a short-term strength of concrete or mortar expressed by a cement composition may become too low in some cases. The proportion of the $2\text{CaO}\cdot\text{SiO}_2$ calculated by the Bogue formula is preferably 10% to 25% by mass, more preferably 11% to 23% by mass, and still more preferably 12% to 22% by mass.

[0018]

<Total proportion of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A) and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (C_4AF)>

A total proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and 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 15% to 22% by mass. When the total proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and the $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ calculated by the Bogue formula is less than 15% by mass, since the amount of a liquid phase generated during calcining of cement clinker is reduced, a solid-phase-liquid phase reaction due to liquid phase intervention may not proceed rapidly, and the cement

clinker may be insufficiently calcined in some cases. In addition, since dust is scattered during cement kiln and radiant heat from a burner is blocked, the cement clinker may not be calcined efficiently in some cases. In addition, when the total proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and the $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ calculated by the Bogue formula is more than 22% by mass, since poor operation is likely to occur, and at the same time and production of calcium silicate minerals that contribute to strength is reduced, the strength of a cement composition using the cement clinker of the present invention may be reduced in some cases. In addition, heat of hydration of a cement composition may become too high in some cases. The total proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and the $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ calculated by the Bogue formula is preferably 17% to 22% by mass, more preferably 18% to 22% by mass, and still more preferably 18% to 20% by mass.

[0019]

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

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 5.5% to 12.5% by mass, more preferably 7% to 12% by mass, and still more preferably 8% to 11% by mass. When the proportion of the $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ calculated by the Bogue formula is within the above range,

a decrease in viscosity of the liquid phase generated during calcining of the cement clinker is suppressed, and granulation of the cement clinker is appropriately proceeded, because it is possible to suppress a layer

5 pressure in a clinker cooler from becoming inconsistent due to a reduction in a particle size of the cement clinker and to reduce the heat of hydration. When the layer pressure in the clinker cooler is not constant, interference with quenching of cement clinker may occur in some cases.

10 [0020]

<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 8.5% to 12.5% by mass, more
15 preferably 9.0% to 11.5% by mass, and still more preferably 9.5% to 11.0% by mass. When 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 is within the above range, the strength exhibited by the cement composition can be further increased and the heat of
20 hydration can be further reduced.

[0021]

<Trace components>

The cement clinker of the present invention contains MgO , TiO_2 , MnO , and ZnO , as trace components. Each content
25 of the MgO , the TiO_2 , and the MnO is measured in accordance

with JIS R 5204:2019 "Analysis method for cement by X-ray fluorescence". The content of the ZnO is measured in accordance with JCASI-53: 2018 "method for quantifying trace components in cement".

5 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 TiO₂ is introduced into the cement clinker, for example, by using titanium gypsum or fly ash as a raw
10 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.

 The ZnO is introduced into the cement clinker, for
15 example, by using municipal waste incineration ash as a raw material for the cement clinker.

[0022]

<Content of MgO>

 In the present invention, the content of the MgO in
20 the cement clinker is preferably 0.50% to 2.00% by mass, more preferably 0.80% to 1.80% by mass, and still more preferably 0.95% to 1.60% by mass. When the content of the MgO is within the above range, the cement clinker can be calcined well and hydration expansion during hardening of
25 concrete or mortar can be suppressed.

[0023]

In the cement clinker of the present invention, each content rate (% by mass) of the MgO, the TiO₂, the MnO, and the ZnO in 3CaO·Al₂O₃ satisfies the following formula (1).

$$C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$$

$C_{\text{Mg-C3A}}$: Content rate (% by mass) of MgO in 3CaO·Al₂O₃

$C_{\text{Ti-C3A}}$: Content rate (% by mass) of TiO₂ in 3CaO·Al₂O₃

$C_{\text{Mn-C3A}}$: Content rate (% by mass) of MnO in 3CaO·Al₂O₃

$C_{\text{Zn-C3A}}$: Content rate (% by mass) of ZnO in 3CaO·Al₂O₃

In formula (1), $C_{\text{Mg-C3A}}$, $C_{\text{Ti-C3A}}$, $C_{\text{Mn-C3A}}$, and $C_{\text{Zn-C3A}}$ each represent a content rate of each component contained in C₃A in an actual cement clinker. Formula (1) can be obtained by multiple regression analysis.

[0024]

The $C_{\text{Mg-C3A}}$, the $C_{\text{Ti-C3A}}$, the $C_{\text{Mn-C3A}}$, and the $C_{\text{Zn-C3A}}$ can be determined by the following steps. First, the cement clinker is subjected to a predetermined treatment, and a composition image of the cement clinker particle is observed with an electron probe microanalyzer (EPMA). In the composition image, each mineral is specified based on the following characteristics.

(a) C₃S: Polygonal particle, light gray, and tens of μm in size

(b) C₂S: Elliptical particle, dark gray, and tens of μm in size

(c) C₃A: Amorphous structure found between particles identified as C₃S and C₂S, dark gray, several μm to a dozen μm in size

(d) C₄AF: Amorphous structure found between particles
5 identified as C₃S and C₂S, white, several μm to a dozen μm in size

A characteristic X-ray analysis is performed on the C₃A specified in accordance with the above index using an electron probe microanalyzer (EPMA), and the content rates
10 (% by mass) of the MgO, the TiO₂, the MnO, and the ZnO in the C₃A are determined. In the present invention, the characteristic X-ray analysis is performed on a plurality of points in a region specified as the C₃A in the composition image, and a point where $1.35 < (\text{CaO content rate}) / (\text{Al}_2\text{O}_3 \text{ content rate} + \text{Fe}_2\text{O}_3 \text{ content rate}) < 2.2$ is
15 satisfied is adopted as an analysis point. Then, each average of the measured value of each component at the 20 analysis points is defined as C_{Mg-C3A}, C_{Ti-C3A}, C_{Mn-C3A}, or C_{Zn-C3A}.

20 [0025]

When satisfying Formula (1), a cement clinker having a low heat of hydration can be obtained. The following two points can be considered as the reason for this.

Formula (1) represents that the contents of the MgO,
25 the TiO₂, the MnO, and ZnO in the C₃A are small. It is

presumed that when the amount of the trace components in the C_3A is small, activity of the C_3A decreases, and as a result, the heat of hydration is reduced. From the viewpoint of reducing the heat of hydration, a left side of Formula (1) is preferably 0.0008 or less. On the other hand, the left side of Formula (1) is preferably 0.0001 or more from the viewpoint of securing the activity of the C_3A to some extent and preventing a delay in setting time of mortar or concrete.

10 [0026]

Furthermore, a case where the trace components in the C_3A satisfy Formula (1) means that a relatively large amount of Mg, Ti, Mn, and Zn are dissolved in other phases. It is considered that when Mg, Ti, Mn, and Zn are dissolved in the C_4AF , Al is easily incorporated into C_4AF , and precipitation of the C_3A becomes relatively small, because the heat of heat of hydration is reduced.

Although the MnO and the ZnO are extremely trace amount of components in general Portland cement clinker, it is considered that an influence of the heat of hydration on the reduction of the relative precipitation amount of the C_3A or a crystal structure in the C_3A cannot be ignored.

[0027]

In the present invention, the content rate of the Fe_2O_3 in the $3CaO \cdot Al_2O_3$ (C_3A) (hereinafter, may be referred

to as " C_{Fe-C_3A} " in some cases) is preferably less than 6.32% by mass. The C_{Fe-C_3A} is obtained from analysis using an electron probe microanalyzer (EPMA), as the C_{Mg-C_3A} or the like. Specifically, a characteristic X-ray analysis is performed on the C_3A specified by the above steps, using an electron probe microanalyzer (EPMA), and the content rate (% by mass) of the Fe_2O_3 in the C_3A is determined. Moreover, an average of the measured value of each component at 20 analysis points is defined as C_{Fe-C_3A} .

Minerals in an actual cement clinker are formed by solid-dissolving other components with respect to the main components of each phase due to the influence of the above-mentioned trace components or manufacture conditions. Most of the Fe_2O_3 is contained in the C_4AF , but some is also solid-dissolved in the C_3A , the C_3S , and the C_2S . Here, it is presumed as a case where, in a range of a mineral composition represented by Bogue formula, as the content rate of the Fe_2O_3 contained in the C_3A , which is an interstitial phase of actual minerals, is small, the C_3A is difficult to precipitate and the C_4AF is easy to precipitate. That is, the Fe_2O_3 and the Al_2O_3 in the cement clinker are easily consumed for the precipitation of the C_4AF , which leads to a relative reduction in the proportion of the C_3A in the cement clinker. As described above, when the content rate of the Fe_2O_3 in the C_3A is less than 6.32%

by mass, the precipitation of the C_3A , which causes an increase in the heat of hydration is suppressed, and an effect of reducing the heat of hydration can be obtained. The content rate of the Fe_2O_3 in the C_3A is more preferably 5 6.00% by mass or less, still more preferably 5.90% by mass or less, and particularly preferably 5.80% by mass or less.

[0028]

In the present invention, the C_{Ti-C_3A} (content rate of TiO_2 in C_3A) is preferably less than 0.24% by mass. As the 10 content rate of the TiO_2 in the C_3A decreases, the content of the Fe_2O_3 in the C_3A also tends to decrease. Therefore, the proportion of the C_4AF in the cement clinker tends to increase relatively, and the proportion of the C_4AF tends to decrease. When the C_{Ti-C_3A} is within the above range, the 15 precipitation of the C_3A can be suppressed and the heat of hydration can be reduced.

[0029]

The chemical composition of the cement clinker in the actual minerals can be adjusted by the chemical composition 20 of the cement clinker, the calcination conditions (heat history) at the time of manufacturing the cement clinker, and the like.

[0030]

In order to make it easier to satisfy Formula (1), for 25 example, each content rate of the Al_2O_3 , the Fe_2O_3 , the MgO ,

the TiO_2 , the MnO , and the ZnO in the cement clinker preferably satisfies Formula (2).

$$C_{\text{Al}_2\text{O}_3} \times (33.06) + C_{\text{Fe}_2\text{O}_3} \times (-8.12) + C_{\text{MgO}} \times (-48.08) + C_{\text{TiO}_2} \times (-163.60) + C_{\text{MnO}} \times (-390.81) + C_{\text{ZnO}} \times (104.60) < 42.9 \dots (2)$$

In Formula (2), $C_{\text{Al}_2\text{O}_3}$ is the content rate (% by mass) of the Al_2O_3 , $C_{\text{Fe}_2\text{O}_3}$ is the content rate (% by mass) of the Fe_2O_3 , C_{MgO} is the content rate (% by mass) of the MgO , C_{TiO_2} is the content rate (% by mass) of the TiO_2 , and C_{MnO} is the content rate (% by mass) of the MnO , and C_{ZnO} is the content rate (% by mass) of the ZnO . The $C_{\text{Al}_2\text{O}_3}$, the $C_{\text{Fe}_2\text{O}_3}$, the C_{MgO} , the C_{TiO_2} , and the C_{MnO} are measured in accordance with JIS R 5204:2019 "Analysis method for cement by X-ray fluorescence", and the C_{ZnO} is measured in accordance with JCAS I-53:2018 "method for quantifying trace components in cement". Formula (2) can be obtained by multiple regression analysis.

[0031]

A coefficient of each section on a left side of Formula (2) corresponds to contribution of the component to the heat of hydration. The formula (2) means that the mineral composition of the interstitial phase changes due to a combined action of the MgO , the TiO_2 , the MnO , and the ZnO which are the trace components. In Formula (2), since the coefficients of the MnO and the ZnO , which are

extremely trace amount of components, are high in general Portland cement clinker, it can be said that the MnO and the ZnO also affect the composition proportion of minerals in the interstitial phase. In the present invention, when
5 the chemical composition of the cement clinker satisfies Formula (2), it becomes easy to satisfy Formula (1).

[0032]

The calcining conditions include a calcining atmosphere, a calcining temperature, a cooling rate, and
10 the like. For example, in a case where the calcining atmosphere is in a reduced state, in a case where the calcining temperature is high, or in a case where the cooling rate is quenching, Formula (1) can be easily satisfied.

15 [0033]

[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
20 Mg, Ti, Mn, and Zn, in addition to Ca, Si, Al, and Fe are used. 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
25 limestone, clay, silica stone, and iron oxide raw

materials. Examples of industrial raw materials include waste raw materials containing the above elements, a blast furnace slag, fly ash, and the like. Regarding a mixing proportion of the clinker raw materials, the composition of the components corresponds to a target value of the Bogue formula, and the raw material blending is determined as in Formula (1) in the cement clinker after calcining. For example, the raw materials are blended because the chemical composition of the cement clinker satisfies Formula (2).

10 [0034]

Then, the clinker raw material mixed in a composition so as to obtain the targeted clinker is calcined under a predetermined 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 calcined at a predetermined first 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 calcining step of heating and calcining, after the temperature raising step, at the predetermined second calcining temperature for a second calcining time. The

temperature and time of each step can be set to obtain the cement clinker after calcining which satisfies Formula (1).

For example, the clinker can be manufactured in a manner that the clinker raw material is heated at a calcining

5 temperature of 950°C to 1100°C (first calcining temperature) for 30 to 60 minutes (first calcining time) to perform calcining (first calcining step), and then temperature is raised to 1420°C to 1480°C (second calcining temperature) over 30 to 60 minutes (temperature raising
10 time) (temperature raising step), and the clinker raw material is further heated at 1420°C to 1480°C for 15 to 45 minutes (second calcining time) to perform calcining (second calcining step), and then a calcined product is quenched.

15 [0035]

[Cement composition]

The cement composition of the present invention contains the cement clinker and gypsum. The Blaine's specific surface area of a mixture of the cement clinker
20 and the gypsum 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>

A proportion of the gypsum in the cement composition
25 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 can be made appropriate, and strength exhibited by the cement composition can be increased. A proportion of SO₃ 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 SO₃ in the cement composition can be determined from a blending amount of the gypsum and the proportion of the SO₃ contained in the gypsum.

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

[0036]

15 <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.

25 [0037]

[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 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.

Examples

10 [0038]

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.

1. Measurement and evaluation

15 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 "Analysis method for cement by X-ray fluorescence" and JCAS I-53:2018 "Quantification method for trace components in cement". 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 1.

25 $C_3S = (4.07 \times CaO) - (7.60 \times SiO_2) - (6.72 \times Al_2O_3) -$

$$(1.43 \times \text{Fe}_2\text{O}_3)$$

$$\text{C}_2\text{S} = (2.87 \times \text{SiO}_2) - (0.754 \times \text{C}_3\text{S})$$

$$\text{C}_3\text{A} = (2.65 \times \text{Al}_2\text{O}_3) - (1.69 \times \text{Fe}_2\text{O}_3)$$

$$\text{C}_4\text{AF} = 3.04 \times \text{Fe}_2\text{O}_3$$

5 Further, the value on the left side of Formula (2) was calculated using the obtained content rate of each component. Results are shown in Table 2.

[0039]

1-2. EPMA measurement

10 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
15 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
20 observed under the following conditions. In the structure image, each mineral was specified based on the characteristics of above (a) to (d).

<EPMA structure image observation conditions>

· Acceleration voltage: 15 kV

25 · Irradiation electric current: 3.0×10^{-8} A

[0040]

Characteristic X-ray analysis was performed on a region identified as the C₃A under the following conditions, and a MgO content rate (% by mass), a TiO₂ content rate (%
 5 by mass), a MnO content rate (% by mass), a ZnO content rate (% by mass), and a Fe₂O₃ content rate (% by mass) in the C₃A were determined.

<EPMA structure image observation conditions>

· Acceleration voltage: 15 kV

10 · Irradiation electric current: 3.0×10^{-8} A

· Beam diameter: Approximately 1 μm

· Correction calculation method: Oxide-ZAF method

The analysis was performed on a plurality of cement clinker particles in the sample, the content rates (% by
 15 mass) of each component at a total of 20 analysis points were obtained, and an average value thereof was calculated as C_{Mg-C3A}, C_{Ti-C3A}, C_{Mn-C3A}, C_{Zn-C3A}, and C_{Fe-C3A} in C₃A.

Furthermore, the value on the left side of Formula (1) was calculated from the obtained content rate of each
 20 component. Results are shown in Table 2.

[0041]

In addition, a characteristic X-ray analysis was performed on the region specified as the C₄AF under the same conditions as above, and the content rate of the Fe₂O₃ in
 25 the C₄AF (% by mass) was determined. In the present

invention, a point where a range within $0.8 < (\text{CaO content rate})/(\text{Al}_2\text{O}_3 \text{ content rate} + \text{Fe}_2\text{O}_3 \text{ content rate}) < 1.35$ was satisfied was adopted as an analysis point, and an average at the 20 analysis points was defined as $C_{\text{Fe-C4AF}}$. Results
 5 are shown in Table 2.

[0042]

1-3. Powder X-ray diffraction measurement

For the cement clinker of Examples and Comparative Examples, X-ray diffraction measurement was performed using
 10 a powder X-ray diffractometer (X'Pert Power, manufactured by Panalysis Ltd.) under measurement conditions of a measurement range: $2\theta = 10^\circ$ to 70° , a step size: 0.017° , scan speed: $0.1012^\circ/\text{s}$, voltage: 45 kV, and an electric current: 40 mA to obtain an X-ray diffraction profile.

15 With respect to the obtained X-ray diffraction profile, cement clinker minerals were quantified using software for crystal structure analysis (X'Pert HighScore Plus version 2.1b, manufactured by Panalysis Ltd.) provided in the powder X-ray diffractometer. The cement clinker
 20 minerals to be analyzed are set to $\text{C}_3\text{S-M1}$ (M1 phase), $\text{C}_3\text{S-M3}$ (M3 phase), $\text{C}_2\text{S-}\alpha'\text{H}$ ($\alpha'\text{H}$ phase), $\text{C}_2\text{S-}\beta$ (β phase), $\text{C}_3\text{A-cubic}$ (cubic crystal), $\text{C}_3\text{A-ortho}$ (orthorhombic crystal), and C_4AF .

A proportion (% by mass) of each mineral of the cement clinker was obtained using an analysis function of Rietveld
 25 method installed in the software, in accordance with Joint

experiment procedure manual 2 of document "Report C-12 of
Cement Chemistry Expert Committee, Examination of
differences in clinker mineral content due to difference in
measurement methods, Part 2, Chapter 4, Examination of

5 Quantification by Powder X-ray Diffraction/Rietveld
Analysis". In addition, a total proportion of each mineral
is 100% by mass, and the content rate of the C_3A (C_{C3A} , % by
mass) and the content rate of the C_4AF (C_{C4AF} , % by mass) in
each of Examples and Comparative Examples was obtained.

10 Results are shown in Table 2.

[0043]

1-4. Measurement of heat of hydration

For the cement of Examples and Comparative Examples,
the heat of hydration at 7 days of age and 28 days of age
15 was measured in accordance with JIS R 5203:2015 "Method for
measuring heat of hydration of cement (heat of dissolution
method)". As reference values, the heat of hydration at 7
days of age was set to 350 J/g, and the heat of hydration
at 28 days of age was set to 400 J/g. Those having a heat
20 of hydration equal to or less than the reference value at
both 7 days of age and 28 days of age were evaluated as
"A", and those exceeding the reference value at any of the
ages were evaluated as "C". Results are shown in Table 2.

[0044]

25 1-5. Mortar compressive strength

For mortar specimens obtained from the mortar of Examples and Comparative Examples, a compressive strength at 3 days of age was measured in accordance with JIS R 5201:2015 "Physical testing methods for cement". Results are shown in Table 2.

[0045]

2. Preparation of cement composition

2-1. Clinker

As raw materials for the cement clinker, calcium 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 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 (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.

5 [0046]

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
10 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 9 and Comparative Examples 1 and 2.

[0047]

15 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
20 cement clinker. The compound was pulverized with a ball mill because 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 9 and Comparative Examples 1 and 2.

25 [0048]

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
5 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. Thereafter, the specimen was cured in water at 20°C until 3 days of age to obtain mortar specimens of each of Examples and
10 Comparative Examples.

[0049]

[Table 1]

	Chemical composition (% by mass)												Mineral 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	ZnO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₃ A+ C ₄ AF
Example 1	21.42	5.85	3.05	65.73	1.46	1.08	0.30	0.40	0.30	0.12	0.09	0.0457	61.1	15.4	10.3	9.3	19.6
Example 2	21.65	5.59	3.43	65.83	1.44	0.53	0.27	0.45	0.32	0.25	0.05	0.0419	60.9	16.2	9.0	10.4	19.4
Example 3	21.35	5.86	3.01	65.64	1.30	1.38	0.32	0.43	0.30	0.12	0.09	0.0471	61.2	15.1	10.4	9.2	19.6
Example 4	21.98	5.66	3.29	65.66	0.99	0.43	0.40	0.35	0.33	0.63	0.09	0.0690	57.4	19.8	9.4	10.0	19.4
Example 5	22.33	5.30	3.56	65.95	0.98	0.49	0.31	0.44	0.27	0.11	0.06	0.0326	58.0	20.4	8.0	10.8	18.9
Example 6	22.05	5.63	3.31	65.71	0.99	0.29	0.38	0.36	0.34	0.65	0.09	0.0750	57.3	20.1	9.3	10.1	19.4
Example 7	21.83	5.35	3.19	66.86	1.03	0.33	0.25	0.44	0.26	0.18	0.08	0.0507	65.7	13.1	8.8	9.7	18.5
Example 8	22.31	5.26	3.55	65.88	0.99	0.60	0.31	0.45	0.27	0.11	0.06	0.0322	58.2	20.2	7.9	10.8	18.7
Example 9	21.77	5.33	3.17	66.86	1.00	0.49	0.24	0.44	0.25	0.18	0.08	0.0509	66.3	12.5	8.8	9.6	18.4
Comparative Example 1	22.30	5.72	3.14	65.99	1.03	0.47	0.26	0.40	0.29	0.15	0.05	0.0348	56.2	21.6	9.9	9.5	19.4
Comparative Example 2	22.26	5.65	3.08	66.41	1.01	0.22	0.30	0.39	0.29	0.15	0.04	0.0436	58.7	19.6	9.8	9.4	19.1

[0050]

[Table 2]

	C _{Mg} -C _{3A} (% by mass)	C _{Ti} -C _{3A} (% by mass)	C _{Mn} -C _{3A} (% by mass)	C _{Zn} -C _{3A} (% by mass)	C _{Fe} -C _{3A} (% by mass)	C _{Fe} -C _{4AF} (% by mass)	Left side of Formula (1)	Left side of Formula (2)	C _{C3A} (% by mass)	C _{C4AF} (% by mass)	Heat of hydration (J/g)			Compressive strength (N/mm ²)
											7 days of age	28 days of age	Determination	
Example 1	0.992	0.150	0.048	0.076	5.00	19.34	0.0005	19.0	6.9	8.8	341	387	A	32.5
Example 2	1.570	0.170	0.020	0.130	5.01	19.55	0.0007	20.2	6.3	9.6	328	377	A	32.1
Example 3	0.900	0.150	0.050	0.070	5.40	20.17	0.0005	27.5	7.6	7.9	333	382	A	31.4
Example 4	0.981	0.159	0.047	0.098	5.48	20.60	0.0007	30.9	8.1	8.3	340	398	A	29.9
Example 5	1.136	0.137	0.036	0.103	5.33	22.17	0.0006	35.0	6.8	9.2	345	395	A	31.5
Example 6	0.960	0.170	0.050	0.100	5.50	20.44	0.0008	28.7	7.8	8.6	338	396	A	29.6
Example 7	0.864	0.155	0.053	0.076	5.61	21.18	0.0005	32.9	6.8	8.3	345	395	A	32.2
Example 8	1.130	0.120	0.030	0.130	5.64	21.21	0.0005	33.2	6.8	9.4	341	386	A	31.7
Example 9	0.880	0.200	0.060	0.070	5.67	20.67	0.0007	35.5	6.6	8.5	345	390	A	31.7
Comparative Example 1	0.940	0.240	0.060	0.090	6.32	21.01	0.0012	50.7	9.0	7.1	353	393	C	30.4
Comparative Example 2	1.006	0.277	0.063	0.092	6.38	20.65	0.0016	54.7	9.5	6.4	351	397	C	31.5

[0051]

In all of Examples 1 to 9, numerical values of Formula (1) was 0.0010 or less, and the heat of hydration was equal to or less than the reference value at both 7 days of age and 28 days of age. On the other hand, in Comparative Examples 1 and 2, the heat of hydration at 7 days of age did not satisfy the reference value. That is, when satisfying Formula (1), a cement composition having a low heat of hydration could be obtained.

[0052]

Focusing on the composition of an interstitial phase of the cement clinker, as shown in Table 2, the content rates of Fe_2O_3 in C_3A of Examples were lower than those of the Comparative Examples. On the other hand, in the present experiment, there was not much correlation between the content rate of the Fe_2O_3 in the C_4AF ($\text{C}_{\text{Fe-C}_4\text{AF}}$) and the content rate ($\text{C}_{\text{Fe-C}_3\text{A}}$) of the Fe_2O_3 in the C_3A . However, it was found that the C_3A content rate in actual minerals by Rietveld analysis tended to be lower in Examples than in Comparative Examples. From this, it can be said that in the cement clinker of Examples, the precipitation of the C_3A was suppressed, and as a result, the heat of hydration was reduced. In Examples 1, 2, 5, and 7 to 9 in which the C_3A content rate by Rietveld analysis was low, the result that the compressive strength at 3 days of age was equal to or

more than that of Comparative Examples was obtained. From this, it can be said that the lower the C_3A content rate by Rietveld analysis, the more the cement composition tends to have excellent short-term strength development.

5 [0053]

In the chemical components shown in Table 1, even in a case where the cement clinker having the same TiO_2 content is used, the heat of hydration according to table 2 is different. As shown in Table 2, it was found that when the
10 C_{Ti-C_3A} was less than 0.24% by mass, the heat of hydration tended to decrease.

CLAIMS

1. A cement clinker comprising:

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

5 formula, of 50% to 75% by mass;

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

formula, of 5% to 25% by mass;

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ in a total proportion,
calculated by Bogue formula, of 15% to 22% by mass;

10 MgO ;

TiO_2 ;

MnO ; and

ZnO ,

wherein Formula (1) is satisfied,

15 $C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$

in Formula (1),

$C_{\text{Mg-C3A}}$ represents a content rate (% by mass) of MgO in

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Ti-C3A}}$ represents a content rate (% by mass) of TiO_2 in

20 $3\text{CaO}\cdot\text{Al}_2\text{O}_3$,

$C_{\text{Mn-C3A}}$ represents a content rate (% by mass) of MnO in

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and

$C_{\text{Zn-C3A}}$ represents a content rate (% by mass) of ZnO in

$3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

25

2. The cement clinker according to claim 1,
wherein a content rate of Fe_2O_3 in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ is less
than 6.32% by mass.

5 3. The cement clinker according to claim 1 or 2,
wherein the content rate of TiO_2 is less than 0.24% by
mass.

4. A cement composition comprising:
10 the cement clinker according to any one of claims 1 to
3; and
gypsum.

5. A method for manufacturing a cement clinker,
15 comprising:
a step of blending raw materials; and
a step of calcining the raw materials blended,
wherein a cement clinker after calcining contains
3CaO·SiO₂ in a proportion, calculated by Bogue
20 formula, of 50% to 75% by mass,
2CaO·SiO₂ in a proportion, calculated by Bogue
formula, of 5% to 25% by mass,
3CaO·Al₂O₃ and 4CaO·Al₂O₃·Fe₂O₃ in a total
proportion, calculated by Bogue formula, of 15% to 22% by
25 mass,

MgO,

TiO₂,

MnO, and

ZnO, and

5 Formula (1) is satisfied,

$$C_{\text{Mg-C3A}} \times C_{\text{Ti-C3A}} \times C_{\text{Mn-C3A}} \times C_{\text{Zn-C3A}} \leq 0.0010 \dots (1)$$

in Formula (1),

$C_{\text{Mg-C3A}}$ represents a content rate (% by mass) of MgO in
3CaO·Al₂O₃,

10 $C_{\text{Ti-C3A}}$ represents a content rate (% by mass) of TiO₂ in
3CaO·Al₂O₃,

$C_{\text{Mn-C3A}}$ represents a content rate (% by mass) of MnO in
3CaO·Al₂O₃, and

$C_{\text{Zn-C3A}}$ represents a content rate (% by mass) of ZnO in
15 3CaO·Al₂O₃.