

SPECIFICATION

Title of Invention

CEMENT COMPOSITION, METHOD FOR PRODUCING SAME, AND METHOD FOR
5 PRODUCING FLY ASH FOR CEMENT COMPOSITION

Technical Field

[0001]

The present invention relates to a cement composition
10 containing fly ash, a method for producing same, and a method
for preparing the fly ash for cement composition.

Background Art

[0002]

15 Fly ash is fine particles that are collected by an
electrical dust collector from fine particles floating in a hot
air flow among burned residues produced when pulverized coal
is burned in a boiler of a coal-fired power plant. Pozzolan
contained in the fly ash, of which major components are silicon
20 dioxide (SiO_2) and aluminum oxide (Al_2O_3), reacts with calcium
hydroxide (Ca(OH)_2) contained in cement to produce a hydrate,
which contributes to long-term strength development of a cured
product. This reaction is called a pozzolanic reaction. Since
the pozzolanic reaction progresses slowly, heat of hydration
25 can be suppressed. Therefore, fly ash is used as an admixture

of concrete or mortar (for example, Patent Literature No. 1).
In addition, fly ash including a large amount of spherical
particles improves workability and thus is used as an admixture
of concrete or mortar (for example, Patent Literature No. 2).

5 [0003]

Fly ash contains spherical particles, which are
spheroidized by a surface tension, and relatively coarse and
porous unburned carbon in the process of burning pulverized coal
in a boiler, exposing burned residues floating in the boiler
10 furnace to a high temperature to melt, and cooling the molten
burned residues. The spherical particles in the fly ash are
vitrified by particle surfaces melting. The relatively coarse
and porous unburned carbon contained in the fly ash has a large
particle diameter. Therefore, it is considered that burning of
15 burned residues does not progress and thus the unburned carbon
does not become spherical particles. The coarse porous unburned
carbon in the fly ash interferes with a ball bearing effect of
the spherical particles, deteriorates fluidity, and causes a
decrease in strength.

20 In addition, in a case where the amount of coarse and porous
unburned carbon in fly ash is large and this fly ash is used
as an admixture, an AE agent added to adjust the air content
is adsorbed on the unburned carbon, and the addition amount of
the AE agent increases, which may lead to an increase in
25 manufacturing costs.

[0004]

The quality of fly ash used as an admixture of concrete or mortar is defined in JIS A6201:2015 "Fly Ash for Use in Concrete". Fly ash from which coarse and porous unburned carbon is removed by classification so as to satisfy the fineness defined in JIS A6201:2015 "Fly Ash for Use in Concrete" is used as an admixture of concrete or mortar.

Prior art Literature

10 Patent Literature

[0005]

[Patent Literature No. 1] Japanese Laid-open Patent Publication No. 2004-292307A

[Patent Literature No. 2] Japanese Laid-open Patent
15 Publication No. 2011-132111A

Summary of Invention

Problems to be solved

[0006]

20 Coarse powder containing unburned carbon, which is classified and produced during the preparing of a standardized fly ash, is landfilled as industrial waste or is used as an alternative material to clay of cement manufacturing raw materials.

25 As the power generation amount increases in a coal-fired

power plant, the amount of fly ash produced in the coal-fired power plant also increases. It is required to efficiently use the entire amount of fly ash which is increasingly produced from a coal-fired power plant without removal of some of the fly ash.

5 [0007]

Therefore, an object of the present invention is to provide a cement composition contributing to long-term strength development, a method for producing same, and a method for preparing fly ash for a cement composition, the fly ash is capable
10 of maintaining properties as an admixture such as improvement of fluidity or contribution to strength development, and the entire amount of raw material fly ash obtained from a coal-fired power plant or the like as an admixture without removal of coarse powder by classification can be used.

15

Solution to Problems

[0008]

The present inventors performed a thorough investigation in order to achieve the object and found that, in a case where
20 fly ash satisfies the following Expression (I) in a volume-based particle diameter distribution of particles contained in the fly ash, the fly ash is capable of maintaining properties as an admixture such as fluidity or strength development, the entire amount of raw material fly ash obtained from a coal-fired power
25 plant or the like can be used as an admixture, and the fly ash

contributes to long-term strength development, thereby completing the present invention. That is, the present invention is as follows.

[0009]

5 [1] A cement composition including:

cement; and

fly ash,

in which a fly ash content is 30 mass% or lower, and

10 the fly ash satisfies the following Expression (I) in a volume-based particle diameter distribution,

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$$

(where D10, D50, and D90 represent particle diameters corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90% in order
15 from the smallest diameter of the fly ash).

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

in which the fly ash content is 12 mass% or higher.

[3] The cement composition according to [1] or [2],

in which the amount of an amorphous phase in the fly ash
20 is 55 mass% or higher with respect to the total amount of a crystal phase and the amorphous phase in the fly ash. In this specification, the amount (mass%) of the amorphous phase in the fly ash refers to a value obtained by subtracting the amount (mass%) of unburned carbon from the amount (mass%) of an
25 amorphous phase obtained by Rietveld analysis described below.

[4] The cement composition according to any one of [1] to [3],

in which the amount of Fe in the amorphous phase of the fly ash is 3.5 mass% or higher and 10 mass% or lower.

5 [5] The cement composition according to any one of [1] to [4],

in which the amount of unburned carbon in the fly ash is 3 mass% or higher and 15 mass% or lower.

[6] The cement composition according to any one of [1] to [5],

in which a Blaine specific surface area of the fly ash is 3000 cm²/g or higher and 4500 cm²/g or lower.

[7] The cement composition according to any one of [1] to [6],

15 in which the amount of unburned carbon having a particle diameter of more than 212 μm is 1.5 mass% or lower.

[8] The cement composition according to any one of [1] to [7],

in which a mass ratio of the unburned carbon having a particle diameter of more than 212 μm in the fly ash to the unburned carbon in the fly ash is 35 mass% or lower.

[9] A method for preparing fly ash for a cement composition, the method including:

classifying coarse powder fly ash having a particle diameter of 45 μm or more from raw material fly ash;

crushing the classified coarse powder fly ash; and
mixing the raw material fly ash and the crushed fly ash
with each other so as to satisfy the following Expression (I)
in a volume-based particle diameter distribution,

5 $0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$

(where D10, D50, and D90 represent particle diameters
corresponding to a cumulative frequency of 10%, a cumulative
frequency of 50%, and a cumulative frequency of 90% in order
from the smallest diameter of the fly ash respectively).

10 [10] A method for producing cement including:

classifying coarse powder fly ash having a particle
diameter of 45 μm or more from raw material fly ash;

crushing the classified coarse powder fly ash;

mixing the raw material fly ash and the crushed fly ash
15 with each other so as to satisfy the following Expression (I)
in a volume-based particle diameter distribution; and

adding the mixed fly ash such that the amount thereof is
30 mass% or lower with respect to the total amount of the cement
composition,

20 $0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$

(where D10, D50, and D90 represent particle diameters
corresponding to a cumulative frequency of 10%, a cumulative
frequency of 50%, and a cumulative frequency of 90% in order
from the smallest diameter of the fly ash respectively).

25 [11] The method for producing a cement composition

according to [10],

in which the mixed fly ash is added such that the amount thereof is 12 mass% or higher with respect to the total amount of the cement composition.

5 [12] The method for producing a cement composition according to [10] or [11],

in which the amount of an amorphous phase in the mixed fly ash is 55 mass% or higher with respect to the total amount of a crystal phase and the amorphous phase in the mixed fly ash.

10 [13] The method for producing a cement composition according to any one of [10] to [12],

in which the amount of Fe in the amorphous phase of the mixed fly ash is 3.5 mass% or higher and 10 mass% or lower.

15 Effects of Invention

[0010]

According to the present invention, a cement composition contributing to long-term strength development, a method for producing same, and a method for preparing fly ash for a cement
20 composition can be provided, the fly ash is capable of maintaining properties as an admixture such as improvement of fluidity or contribution to strength development, and the entire amount of raw material fly ash obtained from a coal-fired power plant or the like as an admixture without removal of coarse powder
25 by classification can be used.

Mode for carrying out the Invention

[0011]

Hereinafter, the present invention will be described.

A cement composition of one embodiment of the present
5 invention comprises cement and fly ash, in which a fly ash content
is 30 mass% or lower, and the fly ash satisfies the following
Expression (I) in a volume-based particle diameter
distribution.

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I)$$

10 (In the expression, D10, D50, and D90 represent particle
diameters corresponding to a cumulative frequency of 10%, a
cumulative frequency of 50%, and a cumulative frequency of 90%
in order from the smallest diameter of the fly ash respectively).

[0012]

15 Fly Ash

The fly ash produced from a coal-fired power plant or the
like contains spherical particles, which are spheroidized by
a surface tension, and relatively coarse and porous unburned
carbon in the process of burning burned residues and cooling
20 the molten burned residues.

[0013]

Ratio $(D50 - D10) / (D90 - D50)$ in Volume-based Particle
Diameter Distribution

The fly ash contained in the cement composition satisfies
25 Expression (I) in the volume-based particle diameter

distribution. Expression (I) represents a ratio of a value which is obtained by subtracting a particle diameter D10 corresponding to a cumulative frequency of 10% from a particle diameter D50 (median diameter) corresponding to a cumulative frequency of 50%, to a value which is obtained by subtracting the particle diameter D50 from a particle diameter D90 corresponding to a cumulative frequency of 90%, in the volume-based particle diameter distribution of the fly ash, the cumulative frequencies being the values in order from the smallest diameter.

By setting the ratio represented by $(D50-D10)/(D90-D50)$ in the volume-based particle diameter distribution of the fly ash to be higher than 0.24 and 0.5 or lower as expressed by Expression (I), the volume-based particle diameter distribution of the fly ash shows a bilaterally symmetric normal distribution with respect to the diameter D50 (median diameter) and more specifically shows a distribution having a slightly broad shape in the right side (side of particles having a particle diameter more than the particle diameter D50). In addition, by setting the ratio represented by $(D50-D10)/(D90-D50)$ in the volume-based particle diameter distribution of the fly ash to be higher than 0.24 and 0.5 or lower, the volume-based particle diameter distribution shows a distribution having a sharp shape. The fly ash contained in the cement composition has the ratio represented by Expression (I) in the volume-based particle

diameter distribution. As a result, the amount of coarse powder in the fly ash can be reduced, deterioration in fluidity or strength development caused by a large amount of coarse and porous unburned carbon can be suppressed, and superior fluidity and strength development of the cement composition to which the fly ash is added can be maintained.

In this specification, the volume-based particle diameter distribution of the fly ash can be measured using a laser diffraction particle size analyzer (for example, MICROTRAC MT2000, manufactured by Nikkiso Co., Ltd.).

[0014]

In a case where the ratio represented by $(D50-D10)/(D90-D50)$ of Expression (I) in the fly ash contained in the cement composition in the volume-based particle diameter distribution is higher than 0.5, the proportion of fine particles increases, the setting time of the cement composition is reduced, and workability may deteriorate. In a case where the ratio represented by $(D50-D10)/(D90-D50)$ of Expression (I) in the fly ash contained in the cement composition in the volume-based particle diameter distribution is 0.24 or lower, the proportion of coarse particles increases, fluidity deteriorates, and strength development may deteriorate.

[0015]

The ratio $[(D50-D10)/(D90-D50)]$ of the value obtained by subtracting the particle diameter D10 from the particle diameter

D50 to the value obtained by subtracting the particle diameter D50 from the particle diameter D90 is preferably 0.25 or higher and 0.49 or lower, more preferably 0.26 or higher and 0.48 or lower, and still more preferably 0.27 or higher and 0.47 or lower.

5 [0016]

The particle diameter D50 is preferably 17~26 μm and more preferably 18~25 μm . In the fly ash in which the particle diameter D50 is in a range of 17~26 μm and a relationship between the particle diameter D50, the particle diameter D10, and the particle diameter D90 satisfies Expression (I) in the volume-based particle diameter distribution, the amount of coarse powder in the fly ash can be reduced, deterioration in fluidity or strength development caused by a large amount of coarse and porous unburned carbon can be suppressed, and superior fluidity and strength development of the cement composition to which the fly ash is added can be maintained.

[0017]

The particle diameter D10 is preferably 4~12 μm and more preferably 5~10 μm . In addition, the particle diameter D90 is preferably 50~69 μm and more preferably 52~68 μm . In the fly ash in which a relationship between the particle diameters D10 and D90 and the particle diameter D50 satisfies Expression (I) in the volume-based particle diameter distribution, deterioration in fluidity or strength development caused by a

large amount of coarse and porous unburned carbon can be suppressed, and superior fluidity and strength development of the cement composition to which the fly ash is added can be maintained.

5 [0018]

Fly Ash Content in Cement Composition

The fly ash content in the cement composition is 30 mass% or lower, preferably 29 mass% or lower, and more preferably 25 mass% or lower and is preferably 5 mass% or higher, more
10 preferably 10 mass% or higher, and still more preferably 12 mass% or higher.

In a case where the fly ash content in the cement composition is higher than 30 mass%, the fly ash content in the cement composition increases, and the cement content in the
15 cement composition relatively decreases. In a case where the cement content in the cement composition is low, a decrease in strength caused by the low cement content becomes more than the effect of improving strength development obtained by the pozzolanic reaction of the fly ash, and the strength of a cured
20 product may decrease. In a case where the fly ash content in the cement composition is 5 mass% or higher, superior fluidity and strength development of the cement composition can be maintained by adding a fly ash satisfying Expression (I) to the cement composition. In addition, in a case where the fly ash
25 content in the cement composition is 12 mass% or higher, the

setting time can be increased, and workability during construction can be improved.

[0019]

Amount of Amorphous Phase in Fly Ash

5 It is preferable that the amount of an amorphous phase in the fly ash contained in the cement composition is 55 mass% or higher with respect to the total amount of a crystal phase and the amorphous phase in the fly ash. The amorphous phase in the fly ash contains a large amount of pozzolan components (SiO_2 ,
10 Al_2O_3) produced by the pozzolanic reaction, and long-term strength development at a material age of 28 days or 91 days can be improved due to the pozzolanic reaction. Silicon (Si), aluminum (Al), and iron (Fe) contained in the fly ash constitute the amorphous phase containing the elements and crystalline
15 quartz (SiO_2), cristobalite (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; in this specification, also referred to as mullite (3:2)), hematite (Fe_2O_3), or magnetite (Fe_3O_4). The crystal phase in the fly ash does not cause the pozzolanic reaction and does not contribute to long-term strength development. In a case where the amount
20 of the amorphous phase in the fly ash contained in the cement composition is 55 mass% or higher with respect to the total amount of the crystal phase and the amorphous phase in the fly ash, the pozzolan components (SiO_2 , Al_2O_3) presented in the amorphous phase of the fly ash react with calcium hydroxide ($\text{Ca}(\text{OH})_2$)
25 produced by hydration of cement particles. As a result, calcium

silicate hydrate (C-S-H) is sufficiently produced, and long-term strength development can be further improved. The amount of the amorphous phase in the fly ash is more preferably 58 mass% or higher and still more preferably 59 mass% or higher with respect to the total amount of the crystal phase and the amorphous phase in the fly ash. Fly ash in which the amount of an amorphous phase is 100 mass% is not substantially present, and the amount of the amorphous phase in the fly ash is preferably 98 mass% or lower and more preferably 95 mass% or lower with respect to the total amount of the crystal phase and the amorphous phase in the fly ash.

[0020]

The amounts of the crystal phase and the amorphous phase in the fly ash can be measured by Rietveld analysis with a powder X-ray diffractometer. As the powder X-ray diffractometer, for example, D8 Advance (manufactured by Bruker AXS GmbH) can be used. As basic measurement conditions, measurement conditions described below in Examples can be applied.

In addition, in the Rietveld analysis, TOPAS Ver. 4.2 (manufactured by Bruker AXS GmbH) can be used as Rietveld analysis software, and measurement conditions described below in Examples can be applied as Rietveld analysis conditions. Examples of analysis target mineral are quartz, mullite (3:2), anhydrous gypsum, limestone, magnetite, hematite, and titanium dioxide (only a sample added as an internal standard material).

Specifically, the amounts of the crystal phase and the amorphous phase in the fly ash can be measured by Rietveld analysis using a method described in Examples.

In this specification, the amount (mass%) of the amorphous phase in the fly ash refers to a value obtained by subtracting the amount (mass%) of the unburned carbon in the fly ash from the amount (mass%) of the amorphous phase obtained by Rietveld analysis according to the following Expression (1).

Amount (mass%) of Amorphous Phase in Fly Ash=Amount (mass%) of Amorphous Phase obtained by Rietveld Analysis-Amount (mass%) of Unburned Carbon (1)

As the amount (mass%) of the unburned carbon in the fly ash, an ignition loss measured according to JIS A6201 "Fly Ash for Use in Concrete" is obtained.

[0021]

Amount of Fe in Amorphous Phase of Fly Ash

It is preferable that the amount of Fe in the amorphous phase of the fly ash contained in the cement composition is 3.5 mass% or higher and 10 mass% or lower. The amount of Fe in the amorphous phase of the fly ash relates to hydration activity of the amorphous phase at a material age of 28 days. In a case where the amount of Fe in the amorphous phase of the fly ash is 3.5 mass% or higher and 10 mass% or lower, a hydration reaction at a material age of 28 days progresses slowly for a long period of time. Therefore, the calcium silicate hydrate (C-S-H)

produced by the pozzolanic reaction is likely to become more dense, and thus long-term strength development is likely to be further improved. It is preferable that the amount of Fe in the amorphous phase of the fly ash is as high as possible. Typically,
5 there is little case where the amount of Fe in the amorphous phase of the fly ash is higher than 10 mass%. The amount of Fe in the amorphous phase of the fly ash contained in the cement composition is more preferably 3.6 mass% or higher and still more preferably 3.7 mass% or higher.

10 [0022]

Major components of a chemical composition of the fly ash are SiO_2 (about 60~80 mass%) and Al_2O_3 (about 20 mass%), and the SiO_2 - Al_2O_3 amorphous phase (glassy phase) and the crystal phase (for example, mullite (3:2) or quartz) are produced in the fly
15 ash in the process of heating, melting, and cooling during burning in a coal-fired power plant. It is presumed that, in a case where the molten burned residues are more rapidly cooled in the cooling process, the atomic order of the crystal phase in the fly ash is further disordered, and the hydration activity
20 of the amorphous phase (glassy phase) becomes more active. In a case where the burned residues are slowly cooled in the cooling process, and in a case where Fe and the like as impurities are present in the liquid phase forming mullite (3:2), Fe is made to be randomly present in the SiO_2 - Al_2O_3 amorphous phase having
25 the same composition as that of mullite, and the disorder of

the amorphous phase (glassy phase) becomes significant. In a case where the activity of the amorphous phase (glassy phase) increases, strength development generally increases within a short period of time. However, it is presumed that, in a case where the disorder of the amorphous phase (glassy phase) becomes significant due to the presence of Fe, the hydration activity can be slowly maintained for a long period of time, which contributes to an increase in long-term strength.

[0023]

The amount of Fe in the amorphous phase of the fly ash can be calculated from the following Expression (2) by Rietveld analysis and fluorescent X-ray analysis. As described above, the amount (mass%) of the amorphous phase in the fly ash refers to a value obtained by subtracting the amount (mass%) of the unburned carbon in the fly ash from the amount (mass%) of the amorphous phase in the fly ash obtained by Rietveld analysis according to Expression (1).

Amount (mass%) of Fe in Amorphous Phase of Fly Ash= $\left\{ \left(\begin{array}{l} \text{(a) Total Amount (Fluorescent X-Ray Analysis Value) of Fe in Fly} \\ \text{Ash} - \left(\begin{array}{l} \text{(b) Total Amount of Fe in Hematite and Magnetite obtained} \\ \text{by Rietveld Analysis} \end{array} \right) \right) / \left(\begin{array}{l} \text{(c) Amount (mass\% of Amorphous Phase} \\ \text{obtained by Rietveld Analysis)} - \left(\begin{array}{l} \text{(d) Amount (mass\% of Unburned} \\ \text{Carbon)} \end{array} \right) \end{array} \right) \right\} \times 100 \quad (2)$

In Expression (2), (a) the total amount of Fe in the fly ash can be calculated by converting into the amount of Fe using

the following Expression (3) based on a measured value 1 of the amount of Fe (iron oxide (III): Fe_2O_3) in terms of oxides which is measured according to JIS R5204 "Chemical Analysis Method of Cement by X-Ray Fluorescence"

5 (a) Total Amount (mass%) of Fe in Fly Ash=Measured Value
 $1 \times 2\text{Fe}/\text{Fe}_2\text{O}_3$ (111.6/159.7) (3)

In Expression (2), (b) the total amount of Fe in hematite and magnetite obtained by Rietveld analysis can be calculated from the following Expressions (4) and (5) based on a measured
10 value 2 of hematite and a measured value 3 of magnetite which are measured by Rietveld analysis by a method described below in Examples. In addition, (b) the total amount of Fe in hematite and magnetite is the sum of the amount of Fe in hematite and the amount of Fe in magnetite.

15 (c-1) Amount (mass%) of Fe in Hematite=Measured Value
 $2 \times 2\text{Fe}/\text{Fe}_2\text{O}_3$ (111.6/159.7) (4)

 (c-2) Amount (mass%) of Fe in Magnetite=Measured Value
 $3 \times 3\text{Fe}/\text{Fe}_3\text{O}_4$ (167.4/231.5) (5)

[0024]

20 Amount of Unburned Carbon in Fly Ash

The amount of the unburned carbon in the fly ash is preferably 3 mass% or higher and 15 mass% or lower, more preferably 3 mass% or higher and 14.8 mass% or lower, and still more preferably 3 mass% or higher and 14.5 mass% or lower.

25 In a case where the amount of the unburned carbon in the

fly ash is 15 mass% or lower, the fly ash satisfies Expression (I) in the volume-based particle diameter distribution. As a result, superior fluidity and strength development of the cement composition can be maintained. When the amount of the unburned carbon in the fly ash is excessively high, even in a case where the proportion of coarse unburned carbon in the fly ash is low, strength development may deteriorate due to porous unburned carbon. It is preferable that the amount of the unburned carbon in the fly ash is as low as possible. However, typically, fly ash obtained from a coal-fired power plant or the like contains 3 mass% or higher of unburned carbon as long as a part of the unburned carbon is removed by classification or the like. As described above, in this specification, as (d) the amount (mass%) of the unburned carbon in the fly ash, an ignition loss measured according to JIS A6201 "Fly Ash for Use in Concrete" is obtained.

[0025]

Blaine Specific Surface Area of Fly Ash

The Blaine specific surface area of the fly ash is preferably 3000 cm²/g or higher and 4500 cm²/g or lower, is more preferably 3100 cm²/g or higher and 4400 cm²/g or lower, and is still more preferably 3200 cm²/g or higher and 4300 cm²/g or lower.

In a case where the Blaine specific surface area of the fly ash is in a range of 3000 cm²/g or higher and 4500 cm²/g or lower, a ball bearing effect as a property of the fly ash can

be maintained. Further, due to the effect of the fly ash having the particle diameter distribution which satisfies Expression (I), superior fluidity can be maintained, and superior strength development can be maintained.

5 [0026]

Mass Ratio of Unburned Carbon having Particle Diameter of more than 212 μm to Unburned Carbon in Fly Ash

It is preferable that a mass ratio (unburned carbon having a particle diameter of more than 212 μm /unburned carbon) of
10 unburned carbon having a particle diameter of more than 212 μm to the unburned carbon in the fly ash is 35% or lower. The mass ratio of the unburned carbon having a particle diameter of more than 212 μm to the unburned carbon in the fly ash is more preferably 34% or lower, still more preferably 33% or lower,
15 and even still more preferably 32% or lower.

In a case where the mass ratio of the unburned carbon having a particle diameter of more than 212 μm to the unburned carbon in fly ash is 35% or lower, when the fly ash is used in the cement composition, the mass ratio of the coarse and porous unburned
20 carbon in the cement composition is low, and deterioration in fluidity and strength development can be suppressed. It is preferable that the mass ratio (unburned carbon having a particle diameter of more than 212 μm /unburned carbon) of the unburned carbon having a particle diameter of more than 212 μm to the

unburned carbon in the fly ash is as low as possible. In the case of the fly ash which satisfies Expression (I) in the volume-based particle diameter distribution, the mass ratio (unburned carbon having a particle diameter of more than 212 μm /unburned carbon) of the unburned carbon having a particle diameter of more than 212 μm to the unburned carbon in the fly ash is typically 5% or higher.

[0027]

As the amount (mass%) of the unburned carbon having a particle diameter of more than 212 μm in the fly ash, an ignition loss of fly ash remaining on a sieve having an opening of 212 μm can be obtained according to JIS Z8801-1 "Test Sieves Part 1: Test Sieves of Metal Wire Cloth".

[0028]

Mass Ratio of Unburned Carbon having Particle Diameter of more than 212 μm in Cement Composition

It is preferable that the amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition is 1.5 mass% or lower. The amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition is more preferably 1.4 mass% or lower, more preferably 1.3 mass% or lower, and still more preferably 1.2 mass% or lower.

In a case where the amount of the unburned carbon having

a particle diameter of more than 212 μm in the cement composition is 1.5 mass% or lower, the amount of the coarse and porous unburned carbon in the cement composition is low, and deterioration in fluidity and strength development can be suppressed. It is preferable that the amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition is as low as possible. In the case of the fly ash which satisfies Expression (I) in the volume-based particle diameter distribution, the amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition is typically 0.05 mass% or lower.

Regarding the amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition, according to the following Expression (7), the fly ash content (mass%) in the cement composition is multiplied by the amount (mass%) of the unburned carbon having a particle diameter of more than 212 μm in the fly ash, and the obtained value is divided by 100. This value can be calculated as the amount (mass%) of the unburned carbon having a particle diameter of more than 212 μm in the cement composition.

[0029]

Method for preparing Fly Ash for Cement Composition

A method for preparing fly ash for a cement composition according to an embodiment of the present invention comprises:

classifying coarse powder fly ash having a particle diameter of 45 μm or more from raw material fly ash; crushing the classified coarse powder fly ash; and mixing the raw material fly ash and the crushed fly ash with each other so as to satisfy the following Expression (I) in a volume-based particle diameter distribution.

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (\text{I})$$

(where D10, D50, and D90 represent particle diameters corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90% in order from the smallest diameter of the fly ash respectively).

[0030]

The raw material fly ash may satisfy a numerical value of an ignition loss of fly ash Type I, II, or IV described in JIS A6201:2015 "Fly Ash for Use in Concrete".

[0031]

As a method of classifying the coarse powder fly ash having a particle diameter of 45 μm or more from the raw material fly ash, for example, a sieve or an air classifier can be used. The classified coarse powder fly ash having a particle diameter of 45 μm or more can be crushed, for example, using a crusher such as a jet mill, a ball mill, or a bead mill. In a case where the fly ash having a particle diameter of 45 μm or more is crushed, mainly coarse and porous unburned carbon is crushed. As long

as the coarse and porous unburned carbon having a particle diameter of 45 μm or more in the fly ash can be crushed, even in a case where the crushed fly ash and the raw material fly ash are mixed and the mixed fly ash is used for a cement composition, deterioration in fluidity or strength development caused by coarse and porous unburned carbon can be suppressed.

[0032]

Cement

The kind of the cement used in the cement composition is not particularly limited. For example, normal Portland cement, high early strength Portland cement, moderate heat Portland cement, or low-heat Portland cement can be used.

[0033]

Method for producing Cement Composition

A method for producing a cement composition according to one embodiment of the present invention comprises: classifying coarse powder fly ash having a particle diameter of 45 μm or more from raw material fly ash; crushing the classified coarse powder fly ash; mixing the raw material fly ash and the crushed fly ash with each other so as to satisfy the following Expression (I) in a volume-based particle diameter distribution; and adding the mixed fly ash such that the amount thereof is 30 mass% or lower with respect to the total amount of the cement composition.

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (\text{I})$$

(where D10, D50, and D90 represent particle diameters

corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90% in order from the smallest diameter of the fly ash respectively).

[0034]

5 In the method for producing a cement composition, as a method of classifying the coarse powder fly ash having a particle diameter of 45 μm or more from the raw material fly ash, for example, a sieve or an air classifier can be used as in the case of the method for preparing fly ash for a cement composition.

10 The classified coarse powder fly ash having a particle diameter of 45 μm or more can be crushed, for example, using a crusher such as a jet mill, a ball mill, or a bead mill as in the case of the method for preparing fly ash for a cement composition. The crushed fly ash is mixed with the raw material fly ash to

15 satisfy Expression (I) in the volume-based particle diameter distribution, and the mixed fly ash is added such that the amount thereof is 30 mass% or lower with respect to the total amount of the cement composition. As a result, the cement composition can be manufactured.

20 [0035]

 The mixed fly ash in which the raw material fly ash and the crushed fly ash are mixed is added such that the amount thereof is preferably 29 mass% or lower and more preferably 25 mass% or lower and is preferably 5 mass% or higher, more

25 preferably 10 mass% or higher, and still more preferably 12 mass%

or higher with respect to the total amount of the cement composition. In a case where the fly ash content in the cement composition is 12 mass% or higher, the cement composition having a long setting time and superior workability during construction
5 can be obtained.

[0036]

It is preferable that the amount of an amorphous phase in the mixed fly ash in which the raw material fly ash and the crushed fly ash are mixed is 55 mass% or higher with respect to the total
10 amount of a crystal phase and the amorphous phase in the mixed fly ash. In a case where the amount of the amorphous phase in the mixed fly ash is 55 mass% or higher with respect to the total amount of the crystal phase and the amorphous phase in the mixed fly ash, the amount of pozzolan components (SiO_2 , Al_2O_3) in the
15 amorphous phase is high, and the pozzolan components react with calcium hydroxide ($\text{Ca}(\text{OH})_2$) produced by hydration of peripheral cement particles due to the pozzolanic reaction. As a result, calcium silicate hydrate (C-S-H) is likely to be produced, and long-term strength development is likely to be further improved
20 in the obtained cement composition. The amount of the amorphous phase in the mixed fly ash is more preferably 58 mass% or higher and still more preferably 59 mass% or higher and is preferably 98 mass% or lower and more preferably 95 mass% or lower with respect to the total amount of the crystal phase and the amorphous
25 phase in the fly ash. Specifically, the amount of the amorphous

phase in the mixed fly ash can be measured using a method described below in Examples.

[0037]

It is preferable that the amount of Fe in the amorphous phase of the mixed fly ash in which the raw material fly ash and the crushed fly ash are mixed is 3.5 mass% or higher and 10 mass% or lower. The amount of Fe in the amorphous phase of the fly ash relates to hydration activity of the amorphous phase after a material age of 28 days. In a case where the amount of Fe in the amorphous phase of the fly ash is 3.5 mass% or higher and 10 mass% or lower, a hydration reaction after a material age of 28 days progresses slowly for a long period of time. Therefore, the calcium silicate hydrate (C-S-H) produced by the pozzolanic reaction is likely to become more dense, and thus long-term strength development is likely to be further improved. The amount of Fe in the amorphous phase of the fly ash contained in the cement composition is more preferably 3.6 mass% or higher and still more preferably 3.7 mass% or higher.

[0038]

The cement composition may contain an admixture other than the fly ash. Examples of the admixture are blast furnace slag powder, limestone powder, quartz powder, and gypsum.

Examples

[0039]

Next, the present invention will be described in more

detail with Examples but is not limited to the Examples.

[0040]

Preparation of Fly Ash

Fly ashes of Preparing Examples 1 to 7, Reference Preparing
5 Example 1, and Comparative Preparing Examples 2 to 6 were
prepared.

[0041]

(Reference Preparing Example 1)

Fly ash obtained from a coal-fired power plant was used
10 as raw material fly ash.

About 30 vol% of the total amount of raw material fly ash
was classified and removed from the raw material fly ash by a
method using a wire sieve having an opening of 45 μm . As a result,
fly ash satisfying the conditions defined in fly ash Type II
15 for use in concrete of JIS A6201 was prepared. A ratio of the
fly ash used to the raw material fly ash is shown as "Use Ratio
of Fly Ash to Raw Material" in Table 2.

[0042]

(Preparing Examples 1 to 7)

20 Coarse powder having a particle diameter of 45 μm or more
was classified from the raw material fly ash by a turbo classifier
(TC-15N, manufactured by Nisshin Engineering Inc.). The
classified coarse powder fly ash was crushed by a pin-type mill
(free mill, model: M-2, manufactured by Nara Machinery Co., Ltd.)
25 to obtain crushed fly ash. The raw material fly ash and the

crushed fly ash were mixed with each other to satisfy the following Expression (I) in a volume-based particle diameter distribution measured by a laser diffraction particle size analyzer (MICROTRAC MT2000, manufactured by Nikkiso Co., Ltd.),
5 mixed fly ash of Preparing Examples 1 to 7 were obtained.

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I)$$

In Expression (I), D10, D50, and D90 represent particle diameters corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90%
10 in order from the smallest diameter of the fly ash.

Table 1 shows D10, D50, and D90 of each of the fly ash of Preparing Examples 1 to 7 and an ignition loss thereof measured by a method described below. The ignition loss refers to the amount of unburned carbon in the fly ash. In addition, the ratio
15 $(D50 - D10) / (D90 - D50)$ of Expression (I) is shown in Table 2. In the fly of Preparing Example 1 to 7, the entire amount of the raw material fly ash was used as no fly ash was removed. Therefore, "Use Ratio (%) of Fly Ash to Raw Material" in Table 2 is shown as "100%".

20 [0043]

(Comparative Preparing Examples 2 to 6)

Coarse powder having a particle diameter of 45 μm or more was classified from the raw material fly ash by a turbo classifier (TC-15N, manufactured by Nisshin Engineering Inc.). The
25 classified coarse powder fly ash was crushed by a pin-type mill

(free mill, model: M-2, manufactured by Nara Machinery Co., Ltd.) to obtain crushed fly ash. The raw material fly ash and the crushed fly ash were mixed with each other such that the value of $(D50-D10)/(D90-D50)$ of Expression (I) was consistent with value shown in Table 2, in a volume-based particle diameter distribution measured by a laser diffraction particle size analyzer (MICROTRAC MT2000, manufactured by Nikkiso Co., Ltd.), and mixed fly ashes of Comparative Preparing Examples 2 to 6 were obtained.

Table 1 shows D10, D50, and D90 of each of the fly ashes of Comparative Preparing Examples 2 to 6 and an ignition loss thereof measured by a method described below. In addition, the ratio $(D50-D10)/(D90-D50)$ of Expression (I) of each of the fly ash of Comparative Preparing Examples 2 to 6 is shown in Table 2. For the fly ash of Comparative Preparing Examples 2 to 6, the entire amount of the raw material fly ash was used as no fly ash was removed. Therefore, "Use Ratio of Fly Ash to Raw Material" in Table 2 is shown as "100%".

[0044]

[Table 1]

Preparing Example	D10 (μm)	D50 (μm)	D90 (μm)	(D50-D10) / (D90-D50)	Ignition Loss (mass%)
Preparing Example 1	8.9	22.6	65.5	0.32	5.0
Preparing Example 2	7.4	23.5	65.9	0.38	9.5
Preparing Example 3	5.5	21.8	56.5	0.47	14.8
Preparing Example 4	9.9	23.2	51.5	0.47	5.0
Preparing Example 5	7.8	23.1	66.5	0.35	7.0
Preparing Example 6	11.8	23.8	68.1	0.27	5.5
Preparing Example 7	8.4	19.9	66.8	0.25	14.8
Reference Preparing Example 1	8.1	16.5	65.5	0.17	1.9
Comparative Preparing Example 2	9.3	17.9	66.0	0.18	14.5
Comparative Preparing Example 3	9.8	25.9	59.8	0.47	5.0
Comparative Preparing Example 4	6.5	15.5	63.5	0.19	15.5
Comparative Preparing Example 5	7.5	13.5	57.2	0.14	14.9
Comparative Preparing Example 6	5.5	22.5	55.6	0.51	13.0

[0045]

Analysis of Fly Ash

- 5 Each of the fly ash of Preparing Examples 1 to 7, Reference Preparing Example 1, and Comparative Preparing Examples 2 to 6 were prepared as follows. The results are shown in Table 2.

[0046]

(Measurement of Blaine specific surface area)

- 10 The Blaine specific surface area of the obtained fly ash was measured by a Blaine method (method of measuring a specific surface area) described in JIS A6201 "Fly Ash for Use in

Concrete".

[0047]

(Measurement of Amounts (mass%) of Crystal Phase and Amorphous Phase in Fly Ash)

5 The amount (mass%) of a crystal phase and the amount of an amorphous phase in the fly ash were measured by Rietveld analysis using an internal standard material by a powder X-ray diffractometer. As the powder X-ray diffractometer, D8 Advance (manufactured by Bruker AXS GmbH) was used. Measurement
10 conditions, the internal standard material, and Rietveld analysis conditions were as described below.

Measurement Conditions

X-ray bulb: Cu

Tube voltage: 40 kV

15 Tube current: 40 mA

Measurement range of diffraction angle 2θ : start angle=5°, end angle=70°/75°

* In a case where rutile type titanium dioxide was added as the internal standard material and the end angle was 70°, a
20 peak shape of the titanium dioxide at about 70° was not able to be correctly obtained. Therefore, the end angle was set as 75° for a sample to which the titanium dioxide was added.

Step width: 0.025 °/step

Measurement time: 60 sec/step

Internal standard material: rutile type titanium dioxide
[0048]

Rietveld Analysis Conditions

Rietveld analysis software: TOPAS Ver. 4.2 (manufactured
5 by Bruker AXS GmbH)

Zero-point correction: not performed

Correction of height of sample surface: performed

Analysis target mineral: quartz, mullite (3:2), anhydrite,
limestone, magnetite, hematite, and titanium dioxide (only a
10 sample added as an internal standard material) Preferred
orientation function of hematite phase: assuming that preferred
orientation of the hematite phase appears on a diffraction line
of the (110) plane at a diffraction angle 2θ of about 35.5,
refinement was performed using a March-Dollase function with
15 an initial coefficient value as 1. Regarding the magnetite
phase, it was assumed that preferred orientation did not appear.

[0049]

The measurement procedure of the crystal phase such as
magnetite or hematite and the amorphous phase in the fly ash
20 was as described below.

(i) As the internal standard material, fly ash (sample 1)
to which 20 mass% of rutile type titanium dioxide was added,
and fly ash (sample 2) to which no internal standard material
was added were prepared.

25 (ii) The fly ash (sample 2) to which no internal standard

material was added was measured by a powder X-ray diffractometer. Fitting between the obtained power X-ray diffraction pattern of the fly ash (sample 2) and each of theoretical profiles of quartz, mullite (3:2), anhydrite, limestone, magnetite, and hematite as the analysis target minerals was performed to quantitatively analyze the respective analysis target minerals in the fly ash. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software. Regarding magnetite and hematite, the amounts (mass%) of magnetite and hematite in the fly ash were calculated from only the fly ash (sample 2) to which no internal standard material was added.

The reason why the sample 2 to which no internal standard material was added was used for the quantitative analysis of magnetite and hematite is that peaks of magnetite and hematite at a diffraction angle 2θ = around $35.5^{\circ} \sim 35.6^{\circ}$ or less are close to a peak of rutile type titanium dioxide at a diffraction angle 2θ = around 36.1° . In particular, the reason is as follows. In a case where rutile type titanium dioxide having a small particle diameter and a small crystallite size is used as the internal standard material, peak broadening occurs, and the vicinity of the bottom of the peak of rutile type titanium dioxide at a diffraction angle $2\theta = 36.1^{\circ}$ overlaps with the peaks of magnetite and hematite. In particular, in a case where the content of magnetite or hematite is low, there is a large effect on the

value determined by the quantitative analysis.

(iii) The fly ash (sample 1) to which rutile type titanium dioxide was added as the internal standard material was measured by a powder X-ray diffractometer. Fitting between the obtained
5 power X-ray diffraction pattern of the fly ash (sample 1) and each of theoretical profiles of quartz, mullite (3:2), anhydrite, limestone, hematite, magnetite, and titanium dioxide as the analysis target minerals was performed to quantitatively
10 (sample 1) to which the internal standard material was added. Next, the amounts (mass%) of the respective analysis target minerals were calculated by the analysis software.

(iv) Based on the value determined by the quantitative analysis of rutile type titanium dioxide of the sample 1, the
15 total amount G_{total} (mass%) of the amorphous phase containing unburned carbon was calculated from the following Expression (A) .

$$\text{Total Amount } G_{\text{total}} \text{ of Amorphous Phase} = 100 \times (Y - X) / \{ Y \times (100 - X) / 100 \} \quad (\text{A})$$

20 In Expression (A), X represents the addition amount (20 mass%) of the internal standard material, and Y represents the value (mass%) determined by the Rietveld analysis of rutile type titanium dioxide.

(v) The total amount of the amorphous phase was
25 quantitatively analyzed based on the content (mass%) of the

crystal phase of the analysis target minerals in the sample 1.
Next, the content of the crystal phase in consideration of the
total amount of the amorphous phase was calculated based on the
contents (mass%) of the analysis target minerals of the sample

5 2. Crystal Phase (in consideration of Total Amount G_{total} of
Amorphous Phase)=Crystal Phase (Analysis Value of Sample
2) $\times(100-G_{\text{total}})/100$ (B)

In Expression (B), G_{total} represents the total amount (%)
of the amorphous phase determined by the quantitative analysis
10 from Expression (A) based on the analysis value of the sample
1.

(vi) Specifically, according to the following Expression
(1), the content (mass%) of unburned carbon in the fly ash was
subtracted from the total amount G_{total} (mass%) of the amorphous
15 phase calculated from Expression (A), and the obtained value
was set as the amount G_{FA} (mass%) of the amorphous phase in the
fly ash. , An ignition loss measured according to JIS A6201 "Fly
Ash for Use in Concrete" was set as the content (mass%) of the
unburned carbon in the fly ash.

20 Amount G_{FA} (mass%) of Amorphous Phase in Fly Ash=Total
Amount G_{total} (mass%) of Amorphous Phase obtained by Rietveld
Analysis-Content (mass%) of Unburned Carbon (1)

[0050]

(Measurement of Amount (mass%) of Fe in Amorphous Phase
25 of Fly Ash)

The amount of Fe in the amorphous phase of the fly ash was calculated from the following Expression (2) by Rietveld analysis and fluorescent X-ray analysis.

$$\begin{aligned} &\text{Amount (mass\%)} \text{ of Fe in Amorphous Phase of Fly Ash} = \left\{ \left(\begin{aligned} &\text{(a) Total Amount (Fluorescent X-Ray Analysis Value) of Fe in Fly} \\ &\text{Ash} - \left(\begin{aligned} &\text{(b) Total Amount of Fe in Hematite and Magnetite obtained} \\ &\text{by Rietveld Analysis} \end{aligned} \right) \right) / \left(\begin{aligned} &\text{(c) Amount (mass\%) of Amorphous Phase} \\ &\text{obtained by Rietveld Analysis} - \left(\begin{aligned} &\text{(d) Amount (mass\%) of Unburned} \\ &\text{Carbon} \end{aligned} \right) \end{aligned} \right) \right\} \times 100 \quad (2) \end{aligned}$$

In Expression (2), (a) the total amount of Fe in the fly ash can be calculated by converting into the amount of Fe using the following Expression (3) based on a measured value 1 of the amount of Fe (iron oxide (III): Fe_2O_3) in terms of oxides which is measured according to JIS R5204 "Chemical Analysis Method of Cement by X-Ray Fluorescence".

$$\begin{aligned} &\text{(a) Total Amount (mass\%) of Fe in Fly Ash} = \text{Measured Value} \\ &1 \times 2\text{Fe} / \text{Fe}_2\text{O}_3 \quad (111.6 / 159.69) \quad (3) \end{aligned}$$

In Expression (2), (b) the total amount of Fe in hematite and magnetite obtained by Rietveld analysis can be calculated from the following Expressions (4) and (5) based on a measured value 2 of hematite and a measured value 3 of magnetite which are measured by Rietveld analysis by a method described below in Examples. In addition, (b) the total amount of Fe in hematite and magnetite is the sum of the amount of Fe in hematite and the amount of Fe in magnetite.

(c-1) Amount (mass%) of Fe in Hematite=Measured Value
 $2 \times 2\text{Fe} / \text{Fe}_2\text{O}_3$ (111.6/159.69) (4)

(c-2) Amount (mass%) of Fe in Magnetite=Measured Value
 $3 \times 3\text{Fe} / \text{Fe}_3\text{O}_4$ (167.4/231.5) (5)

5 [0051]

(Amount (mass%) of Unburned Carbon in Fly Ash)

As (d) the amount (mass%) of the unburned carbon in the fly ash, an ignition loss measured according to JIS A6201 "Fly Ash for Use in Concrete" was obtained.

10 [0052]

(Amount (mass%) of Unburned Carbon having Particle Diameter of more than 212 μm)

As the amount (mass%) of the unburned carbon having a particle diameter of more than 212 μm in the fly ash, an ignition loss of fly ash remaining on a sieve having an opening of 212 μm can be obtained according to JIS Z8801-1 "Test sieves Part 1: Test sieves of Metal Wire Cloth".

[0053]

20 (Mass Ratio (%) of Unburned Carbon having Particle Diameter of more than 212 μm to Unburned Carbon in Fly Ash)

The mass ratio (unburned carbon having a particle diameter of more than 212 μm /unburned carbon) of the unburned carbon having a particle diameter of more than 212 μm in the fly ash to the unburned carbon in the fly ash was calculated from the

following Expression (6).

Unburned Carbon having Particle Diameter of more than 212 μm /Unburned Carbon (%) = Unburned Carbon (mass%) having Particle Diameter of more than 212 μm in Fly Ash $\div$ Unburned Carbon (mass%) in Fly Ash $\times 100$ (6)

[0054]

Cement Composition

(Examples 1 to 10)

The fly ashes prepared in Preparing Examples 1 to 7 were mixed with normal Portland cement at mixing ratios shown in Table 2, respectively. As a result, cement compositions according to Examples 1 to 10 were manufactured.

[0055]

(Comparative Examples 1 to 6)

The fly ashes prepared in Reference Preparing Example 1 and Comparative Preparing Examples 2 to 6 were mixed with normal Portland cement at mixing ratios shown in Table 2, respectively. As a result, cement compositions according to Comparative Examples 1 to 6 were manufactured.

[0056]

Regarding each of the obtained cement compositions, the mass ratio (%) of the unburned carbon having a particle diameter of more than 212 μm in the cement composition, fluidity, mortar compressive strength, and setting time were measured.

Measurement methods will be described below. In addition, the measurement results are shown in Table 2.

[0057]

(Amount (mass%) of Unburned Carbon having Particle
5 Diameter of more than 212 μm in Cement Composition)

The amount (mass%) of the unburned carbon having a particle diameter of more than 212 μm in the cement composition was calculated from the following Expression (7).

Amount (mass%) of Unburned Carbon having Particle Diameter
10 of more than 212 μm in Cement Composition = Fly Ash Content (mass%)
in Cement Composition $\times$ Amount (mass%) Unburned Carbon having
Particle Diameter of more than 212 μm in Fly Ash $\div 100$ (7)

[0058]

(Fluidity: Evaluation of Fluidity of Mortar)

15 Using the cement compositions containing the fly ash of
each Examples and Comparative Examples, a flow test according
to JIS R5201 "Physical Testing Methods for Cement" was performed
at an environmental temperature of 20°C and at an environmental
temperature of 30°C without using an admixture to measure a flow
20 value of mortar. At an environmental temperature of 20°C, the
fluidity of mortar having a flow value of 180 mm or higher was
evaluated to be high, and the fluidity of mortar having a flow
value of lower than 180 mm was evaluated to be low. At an
environmental temperature of 30°C, the fluidity of mortar having

a flow value of 165 mm or higher was evaluated to be high, and the fluidity of mortar having a flow value of lower than 165 mm was evaluated to be low.

[0059]

5 (Setting Time Test)

Using the cement compositions containing the fly ash of each Examples and Comparative Examples, a setting time test was performed according to Annex A (normative) Setting time test of JIS R5201 "Physical Testing Methods for Cement" except that
10 the temperature of a laboratory where a measurement sample was prepared and a test was performed was set to be $30\pm 2^{\circ}\text{C}$. In a case where the initial setting time of mortar was 110 minutes or longer and the final setting time of mortar was 160 minutes or longer, the setting time was evaluated to be long. In a case
15 where the initial setting time of mortar was shorter than 110 minutes and the final setting time of mortar was shorter than 160 minutes, the setting time was evaluated to be short.

[0060]

(Mortar Compressive Strength at Material Age of 3 Days,
20 Material Age of 28 Days, and Material Age of 91 Days)

Using the cement compositions containing the fly ash of each Examples and Comparative Examples, mortar compressive strength was measured at a material age of 3 days, a material age of 28 days, and a material age of 91 days according to "11.
25 Strength Test" of "JIS R5201 "Physical Testing Methods for

Cement". In a case where the mortar compressive strength at a material age of 3 days was 22 N/mm² or higher, the initial compressive strength of mortar was evaluated to be high. In a case where the mortar compressive strength at a material age of 3 days was lower than 22 N/mm², the initial compressive strength of mortar was evaluated to be low. In a case where the mortar compressive strength at a material age of 28 days was 50 N/mm² or higher, the compressive strength of mortar was evaluated to be high. In a case where the mortar compressive strength at a material age of 28 days was lower than 50 N/mm², the compressive strength of mortar was evaluated to be low. In a case where the mortar compressive strength at a material age of 91 days was 75 N/mm² or higher, the long-term compressive strength of mortar was evaluated to be high. In a case where the mortar compressive strength at a material age of 91 days was lower than 75 N/mm², the long-term compressive strength of mortar was evaluated to be low.

[0061]

[Table 2]

		Fly Ash						Cement Composition									
		Use Ratio of Fly Ash to Raw Material (%)	Blaine specific surface area (cm²/g)	Particle Diameter Ratio (D50-D10)/(D90-D50)	Amount of Amorphous Phase (mass%)	Amount of Unburned Carbon (mass%)	Mass Ratio Amorphous Phase/Unburned Residue (%)	Fly Ash Content (mass%)	Amount of Unburned Carbon having Particle Diameter of more than 212 μm (mass%)	Flow Value (20°C) (mm)	Flow Value (30°C) (mm)	Setting Time Test		Mortar Compressive Strength			
												Initial Setting Time (min)	Final Setting Time (min)				
Example 1	Preparing Example 1	100	3210	0.32	75.1	3.6	5.0	10.0	15	0.1	193	174	110	165	29.5	56.2	79.5
Example 2	Preparing Example 2	100	3210	0.32	75.1	3.6	5.0	10.0	25	0.1	194	174	120	185	24.1	51.7	79.2
Example 3	Preparing Example 3	100	3500	0.38	59.8	6.0	9.5	25.3	20	0.5	189	171	130	190	26.8	54.3	77.5
Example 4	Preparing Example 4	100	3500	0.38	59.8	6.0	9.5	25.3	30	0.7	190	171	135	195	22.6	51.2	79.8
Example 5	Preparing Example 5	100	4300	0.47	65.3	4.4	14.8	30.4	20	0.9	185	167	140	200	26.5	54.3	76.3
Example 6	Preparing Example 6	100	4300	0.47	65.3	4.4	14.8	30.4	29	1.3	184	166	155	210	23.0	50.5	78.1
Example 7	Preparing Example 7	100	3210	0.47	61.3	6.5	5.0	18.0	11	0.1	180	166	75	135	29.5	59.2	78.1
Example 8	Preparing Example 8	100	4100	0.35	65.8	3.3	7.0	12.9	25	0.2	182	169	135	170	22.5	47.9	72.2
Example 9	Preparing Example 9	100	2800	0.27	71.5	3.7	5.5	16.4	25	0.2	196	168	120	170	23.8	47.5	73.8
Example 10	Preparing Example 10	100	3520	0.25	51.5	9.5	14.8	15.5	25	0.6	185	173	155	195	22.3	48.8	71.5
Comparative Example 1	Reference Preparing Example 1	70	3900	0.17	61.5	4.8	1.9	5.3	25	0.0	175	162	115	165	24.4	53.8	75.5
Comparative Example2	Comparative Preparing Example 2	100	3150	0.18	65.1	5.8	14.5	35.9	28	1.5	175	145	160	215	23.2	47.1	73.2
Comparative Example3	Comparative Preparing Example 3	100	3210	0.47	67.3	5.7	5.0	18.0	33	0.3	185	170	145	220	20.5	47.1	75.2
Comparative Example4	Comparative Preparing Example 4	100	4400	0.19	55.1	6.5	15.5	19.4	28	0.8	176	148	155	205	23.0	47.3	73.2
Comparative Example5	Comparative Preparing Example 5	100	3800	0.14	70.1	4.4	14.9	34.9	30	1.6	168	145	160	215	22.6	47.3	75.1
Comparative Example6	Comparative Preparing Example 6	100	4650	0.51	71.5	6.4	13.0	17.7	25	0.6	175	140	100	155	22.8	50.2	79.1

[0062]

As shown in Table 2, in the cement compositions of Examples 1 to 8 using the fly ashes of Preparing Examples 1 to 5 in which the ratio $(D50-D10)/(D90-D50)$ was higher than 0.3 and 0.5 or lower, the flow value at 20°C was superior at 180 mm or higher, the flow value at 30°C was superior at 165 mm or higher, and both the initial mortar compressive strength at a material age of 3 days and the mortar compressive strength at a material age of 28 days were high. In addition, in the cement compositions of Examples 1 to 7, the long-term mortar compressive strength at a material age of 91 days was high at 76.3 N/mm² or higher, and long-term strength development was further improved.

[0063]

In the cement composition of Example 7, the fly ash content of Preparing Example 4 in the cement composition was low at 11 mass%. Therefore, the fluidity and the compressive strength were superior, but the setting time was shorten.

[0064]

In the cement composition of Example 8, the fly ash of Preparing Example 5 was used, and the amount of Fe in the amorphous phase of the fly ash of Preparing Example 5 was low at 3.3 mass%. Therefore, the long-term strength development at a material age of 28 days and a material age of 91 days was lower.

[0065]

In the cement composition of Example 9, the fly ash of

Preparing Example 6 was used, the Blaine specific surface area of the fly ash of Preparing Example 6 was 2800 cm²/g, the amount of coarse powder was relatively large, and the long-term strength development at a material age of 28 days and a material age of 5 91 days was lower.

[0066]

In the cement composition of Example 10, the fly ash of Preparing Example 7 was used, and the amount of the amorphous phase in the amorphous phase of the fly ash of Preparing Example 10 7 was low at 51.5 mass%. Therefore, the long-term strength development at a material age of 28 days and a material age of 91 days was lower.

[0067]

As shown in Table 2, in the fly ash of Reference Preparing 15 Example 1 which was the same as Type II fly ash defined in JIS A6201 "Fly Ash for Use in Concrete", about 30 vol% of the fly ash was necessarily removed from the raw material fly ash in order to satisfy the JIS standard, the ratio of the fly ash used to the raw material fly was 70%, and the entire amount of the 20 raw material fly ash was not efficiently used.

[0068]

As shown in Table 2, in the cement composition of Comparative Example 1, the ratio (D50-D10)/(D90-D50) of the fly ash of Reference Preparing Example 1 was low at 0.17, and the 25 initial mortar compressive strength at a material age of 3 days,

the mortar compressive strength at a material age of 28 days, and the long-term mortar compressive strength at a material age of 91 days were relatively high. However, the flow value at 20°C and the flow value at 30°C did not satisfy the evaluation standard values (20°C: 180 mm or higher; 30°C: 165 mm or higher), and the fluidity was poor.

[0069]

As shown in Table 2, in the cement composition of Comparative Example 2, the ratio $(D50-D10)/(D90-D50)$ of the fly ash of Comparative Preparing Example 2 was low at 0.18, the mass ratio (unburned carbon having a particle diameter of more than 212 μm /unburned carbon) of the unburned carbon having a particle diameter of more than 212 μm to the unburned carbon in the fly ash was higher than 35%, the amount of the coarse porous unburned carbon was high, the fluidity was poor, and the long-term strength development at a material age of 28 days and a material age of 91 days was poor.

[0070]

As shown in Table 2, in the fly ash of Comparative Preparing Example 3 used in Comparative Example 3, the Blaine specific surface area and the ratio $(D50-D10)/(D90-D50)$ were the same as those of the fly ash of Preparing Example 4. The fly ash content in the cement composition was higher than 30 mass%, and the fluidity was good. However, the initial compressive

strength at a material age of 3 days was low, and the mortar compressive strength at a material age of 28 days was low.

[0071]

As shown in Table 2, in the cement composition of Comparative Example 4, the ratio $(D50-D10)/(D90-D50)$ of the fly ash of Comparative Preparing Example 4 was low at 0.19, and the amount of the coarse and porous unburned carbon was relatively high. Therefore, the fluidity at 20°C and the fluidity at 30°C were poor, the mortar compressive strength after a material age of 28 days was low, and the mortar compressive strength after a material age of 91 days was low.

[0072]

As shown in Table 2, in the cement composition of Comparative Example 5, the ratio $(D50-D10)/(D90-D50)$ of the fly ash of Comparative Preparing Example 5 was low at 0.14, and the amount of the unburned carbon having a particle diameter of more than 212 μm in the cement composition was high at 1.6 mass%. Therefore, the amount of the coarse and porous unburned carbon was high, the fluidity at 20°C and the fluidity at 30°C were poor, and the mortar compressive strength at a material age of 28 days was low.

[0073]

As shown in Table 2, in the cement composition of Comparative Example 6, the ratio $(D50-D10)/(D90-D50)$ of the fly ash of Comparative Preparing Example 6 was high at 0.51 which

was higher than 0.5, the Blaine specific surface area was also high at 4650 cm²/g, the amount of relative fine particles in the fly ash was high, and the fluidity at 20°C and the fluidity at 30°C were poor. Further, the setting time at 30°C was short.

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Industrial Applicability

[0074]

According to the present invention, a cement composition capable of contributing to long-term strength development, a method for producing same, and a method for preparing fly ash for a cement composition can be provided using fly ash which is increasingly produced as the power generation amount in a coal-fired power plant increases, the fly ash being capable of maintaining properties as an admixture such as improvement of fluidity or contribution to strength development as an admixture without removal of some of the fly ash.

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CLAIMS

1. A cement composition comprising:

cement; and

5 fly ash,

wherein a fly ash content is 30 mass% or lower, and

the fly ash satisfies the following Expression (I) in a
volume-based particle diameter distribution,

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$$

10 (where D10, D50, and D90 represent particle diameters
corresponding to a cumulative frequency of 10%, a cumulative
frequency of 50%, and a cumulative frequency of 90% in order
from the smallest diameter of the fly ash).

15 2. The cement composition according to claim 1,
wherein the fly ash content is 12 mass% or higher.

3. The cement composition according to claim 1 or 2,
wherein the amount of an amorphous phase in the fly ash
20 is 55 mass% or higher with respect to the total amount of a crystal
phase and the amorphous phase in the fly ash.

4. The cement composition according to any one of claims
1 to 3,

25 wherein the amount of Fe in the amorphous phase of the fly

ash is 3.5 mass% or higher and 10 mass% or lower.

5. The cement composition according to any one of claims
1 to 4,

5 wherein the amount of unburned carbon in the fly ash is
3 mass% or higher and 15 mass% or lower.

6. The cement composition according to any one of claims
1 to 5,

10 wherein a Blaine specific surface area of the fly ash is
3000 cm²/g or higher and 4500 cm²/g or lower.

7. The cement composition according to any one of claims
1 to 6,

15 wherein the amount of unburned carbon having a particle
diameter of more than 212 μm in the cement composition is 1.5
mass% or lower.

8. The cement composition according to any one of claims
20 1 to 7,

wherein a mass ratio of the unburned carbon having a
particle diameter of more than 212 μm in the fly ash to the
unburned carbon in the fly ash is 35 mass% or lower.

25 9. A method for preparing fly ash for a cement composition,

the method comprising:

classifying coarse powder fly ash having a particle diameter of 45 μm or more from raw material fly ash;

crushing the classified coarse powder fly ash; and

5 mixing the raw material fly ash and the crushed fly ash with each other so as to satisfy the following Expression (I) in a volume-based particle diameter distribution,

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$$

(where D10, D50, and D90 represent particle diameters
10 corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90% in order from the smallest diameter of the fly ash respectively).

10. A method for producing a cement composition:

15 classifying coarse powder fly ash having a particle diameter of 45 μm or more from raw material fly ash;

crushing the classified coarse powder fly ash;

mixing the raw material fly ash and the crushed fly ash with each other so as to satisfy the following Expression (I)
20 in a volume-based particle diameter distribution; and

adding the mixed fly ash such that the amount thereof is 30 mass% or lower with respect to the total amount of the cement composition,

$$0.24 < (D50 - D10) / (D90 - D50) \leq 0.5 \quad (I),$$

(where D10, D50, and D90 represent particle diameters corresponding to a cumulative frequency of 10%, a cumulative frequency of 50%, and a cumulative frequency of 90% in order from the smallest diameter of the fly ash respectively).

5

11. The method for producing a cement composition according to claim 10,

wherein the mixed fly ash is added such that the amount thereof is 12 mass% or higher with respect to the total amount
10 of the cement composition.

12. The method for producing a cement composition according to claim 10 or 11,

wherein the amount of an amorphous phase in the mixed fly
15 ash is 55 mass% or higher with respect to the total amount of a crystal phase and the amorphous phase in the mixed fly ash.

13. The method for producing a cement composition according to any one of claims 10 to 12,

20 wherein the amount of Fe in the amorphous phase of the mixed fly ash is 3.5 mass% or higher and 10 mass% or lower.